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METHODS AND PROCEDURES UTILIZED IN ENVIRONMENTAL MANAGEMENT ACTIVITIES AT OAK RIDGE NATIONAL LABORATORY

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ABSTRACT

The Department of Environmental Management at Oak Ridge National Laboratory have established an environmental monitoring program which includes sampling and analyzing air, water, terrestrial and biological indicators for radioactive and nonradioactive pollutants.

The concentration of airborne particulates in the general area is monitored by local air monitoring stations, perimeter air monitoring stations and/or remote air monitoring stations. Radioactive particulates are monitored by passing air continuously through filter paper. Airborne radioactive iodine is monitored by passing air continuously through a charcoal cannister. Fallout particulates are captured on gummed paper and analyzed for radioactivity. External gamma radiation is determined by using thermoluminescent dosimeters of various sizes. The external gamma radiation is also determined at the Burial Ground, ORGDP, and ORNL in the same manner.

The concentration of radionuclides in water is determined by analyzing samples collected from White Oak Creek, White Oak Dam, and other waterways (Gallaher, Melton Hill, Kingston, and the faucet). Rainwater is analyzed for washout; other samples collected from Melton Branch, Sewage Treatment Plant, and White Oak Creek are analyzed for pollutants for the National Pollutant Discharge Elimination System.

Terrestrial and biological samples are collected and analyzed for elemental and radionuclide concentrations. These samples include grass, soil, deer, fish, and foodstuff.

This manual has been compiled to familiarize all employees of the Department of Environmental Management with the collection, preparation, and analyses of these samples. Procedures are presented for all samples; therefore, the content of this manual will be revised with the elimination and establishment of projects and procedures.

INTRODUCTION

This manual has been prepared by the staff of the Department of Environmental Management (DEM) of the Industrial Safety and Applied Health Physics Division (IS&AHP) at Oak Ridge National Laboratory (ORNL) in an effort to promote uniformity among methods of analyzing air, water, terrestrial, and biological samples. This manual may also be beneficial during the absence of regularly employed technicians. It should be noted that the methods used by the DEM are evolving, and through these procedures will be updated periodically.

DISCLAIMER

This manual, entitled "Methods and Procedures Utilized in Environmental Management Activities at Oak Ridge National Laboratory," is intended as a bench-top working manual and, therefore, contains a considerable amount of detail that would not normally be in such a manual. It is intended that as procedures are upgraded, the changed procedures will be transmitted to those on the distribution list.

SUMMARY TABLE

Samples are collected by the staff of the Department of Environmental Management weekly, monthly, quarterly, semiannually, and/or annually. The samples are analyzed and the data are recorded in various reports. The frequency of sample collection, size and number of samples, analyses, results and other pertinent data are presented in the Summary Table.

1. AIR SAMPLING

The staff of the Department of Environmental Management monitors airborne pollutants (both radioactive and nonradioactive) in local, perimeter, and remote areas of Oak Ridge National Laboratory (ORNL). There are 23 local air monitoring (LAM) stations, 9 perimeter air monitoring (PAM) stations, and 7 remote air monitoring (RAM) stations. Although the monitoring facilities are different for the three types of stations (as will be detailed later), most of the stations provide for the collection of (1) airborne radioactive particulates by air filtration techniques, (2) radioactive particulate fallout materials by impingement on gummed paper trays, (3) rainwater for measurements of fallout occurring as rainout, and (4) iodine-131 using charcoal cartridges. High volume air samplers and tritium monitors have also been installed at several LAM stations. External gamma radiation background is measured at all stations using thermoluminescent dosimeters (TLDs).

1.1 Sample Collection at Local Air Monitoring (LAM) Stations

A LAM station is shown in Fig. 1.1-1. Both the LAM and PAM stations have provisions for telemetering some of their data to a central monitoring (CM) panel board and alarm systems located in Building 4500-South, Rm H-251 (Figs. 1.1-2 through 1.1-3). The LAM stations contain a moving filter (roll of Whatman No. 41 filter paper) radioactive monitor. The output of the Geiger-Mueller (G-M) detector, which is used to monitor the moving filter, is telemetered to the CM facilities for continuous readout.

Located at the LAM stations is a fallout monitoring system which consists of a continuously turning (at a rate of 1 rpm) circular disk on top of the station. The alpha and beta detectors are located a few millimeters above the disk, and the output of the detectors is continuously telemetered to the CM facility.

A Hollingsworth and Vose LB-5211 filter paper (12.5 by 12.5 cm) is used for sampling air activity at the LAM stations (Fig. 1.1-4). Unlike at the PAM stations, there is no G-M detector associated with the filter. Two air pressure regulators are incorporated in the air pumping system to aid in keeping the flow rates constant for the moving filter and the LB-5211 filter.

Collection of iodine-131 in the atmosphere is performed by the adsorption of gaseous iodine on an activated charcoal cannister (6-14 mesh charcoal). This cannister is located downstream from the Vose LB-5211 particulate filter. The collection efficiency for particulate iodine is greater than 99%; the collection efficiency for methyl iodine is greater than 60%, depending on such factors as the relative humidity.

Particulate fallout in the air is collected on a 0.30- by 0.30-m gummed cellulose acetate paper. The gummed paper, adhered to a steel frame, is placed on the air monitoring station parallel to the ground. The gummed paper is analyzed at ORNL using autoradiography (for LAMs only) and counted by a scintillation counter for gross beta activity.

Long-term exposures of radiation are also monitored at each site using Harshaw TLD-100s or -200s. The TLD chips are placed in polyethylene containers and attached to the air monitor shelter. The containers are

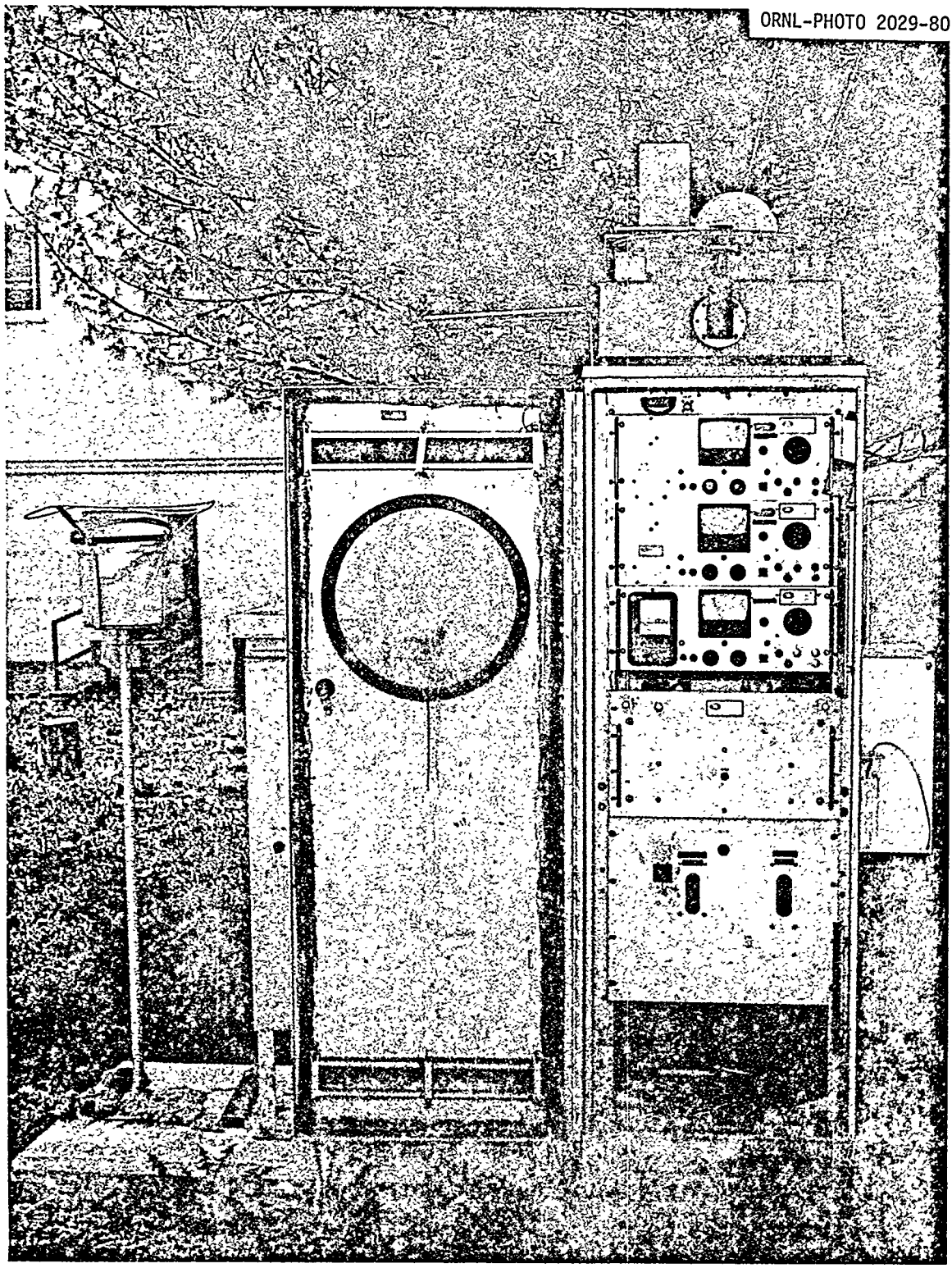

Fig. 1.1-1. A LAM station.

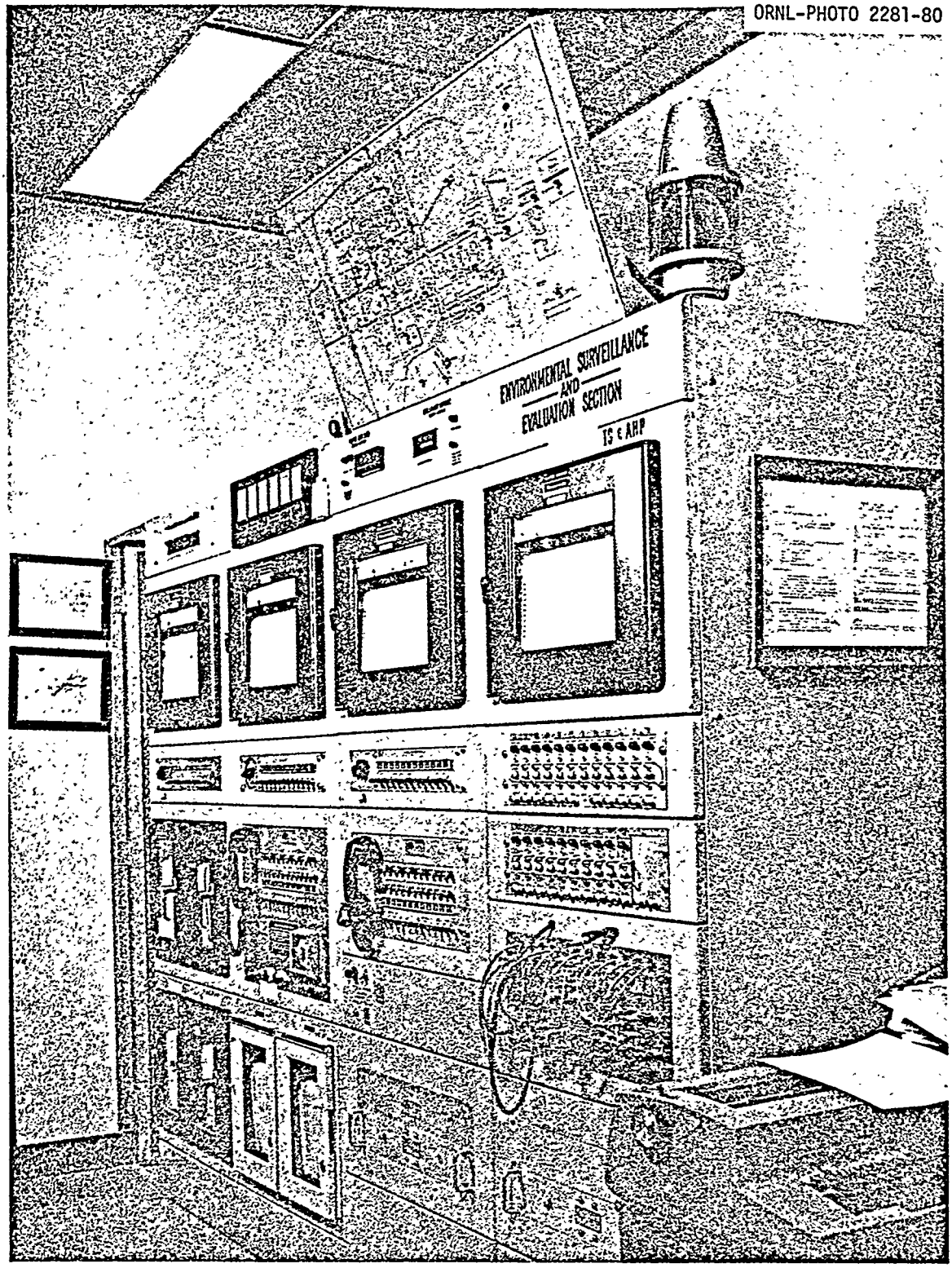

Fig. 1.1-2. Data are telemetered and displayed on panel boards.

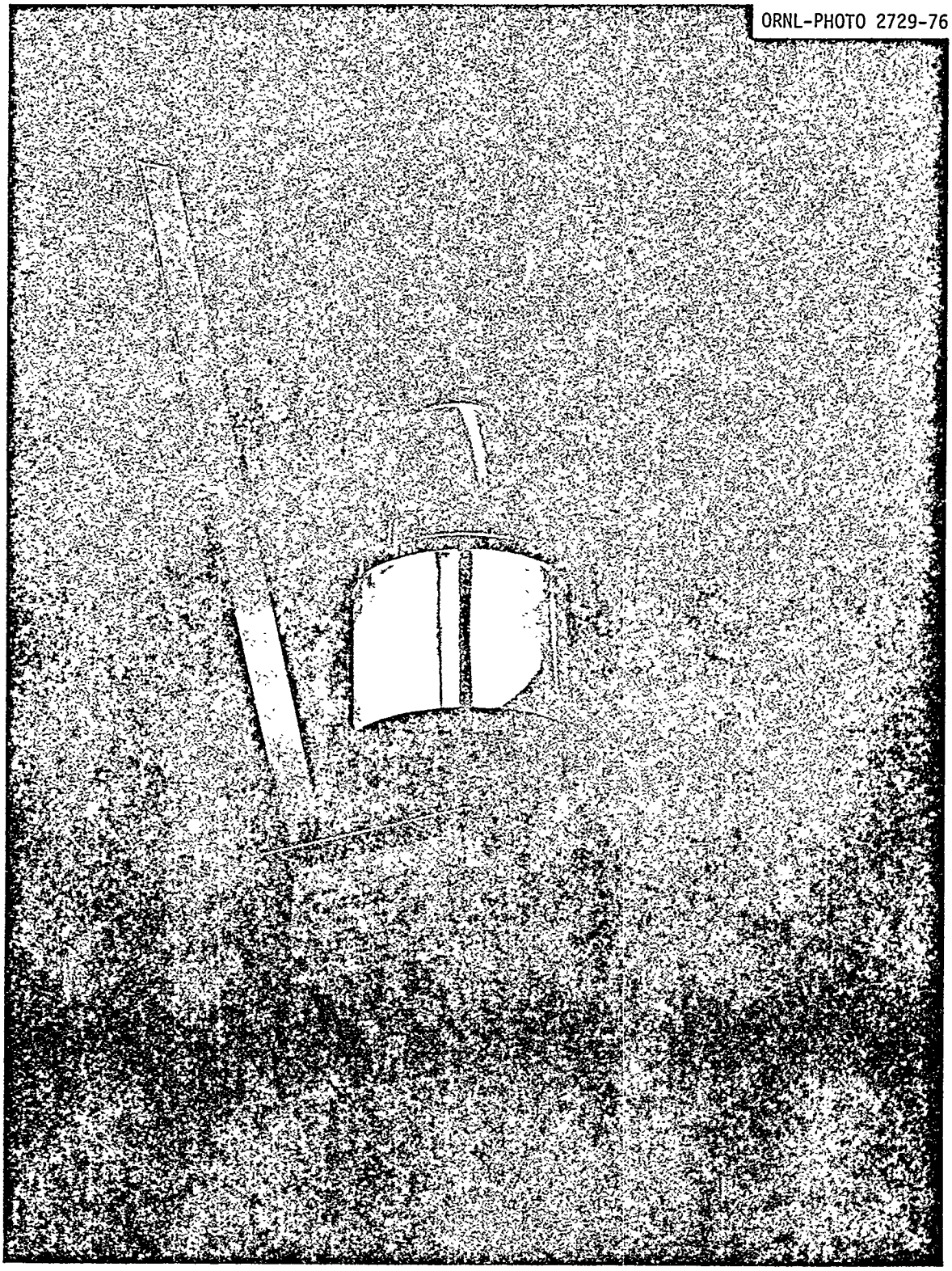

Fig. 1.1-3. Indicator light on telecommunication panel board.

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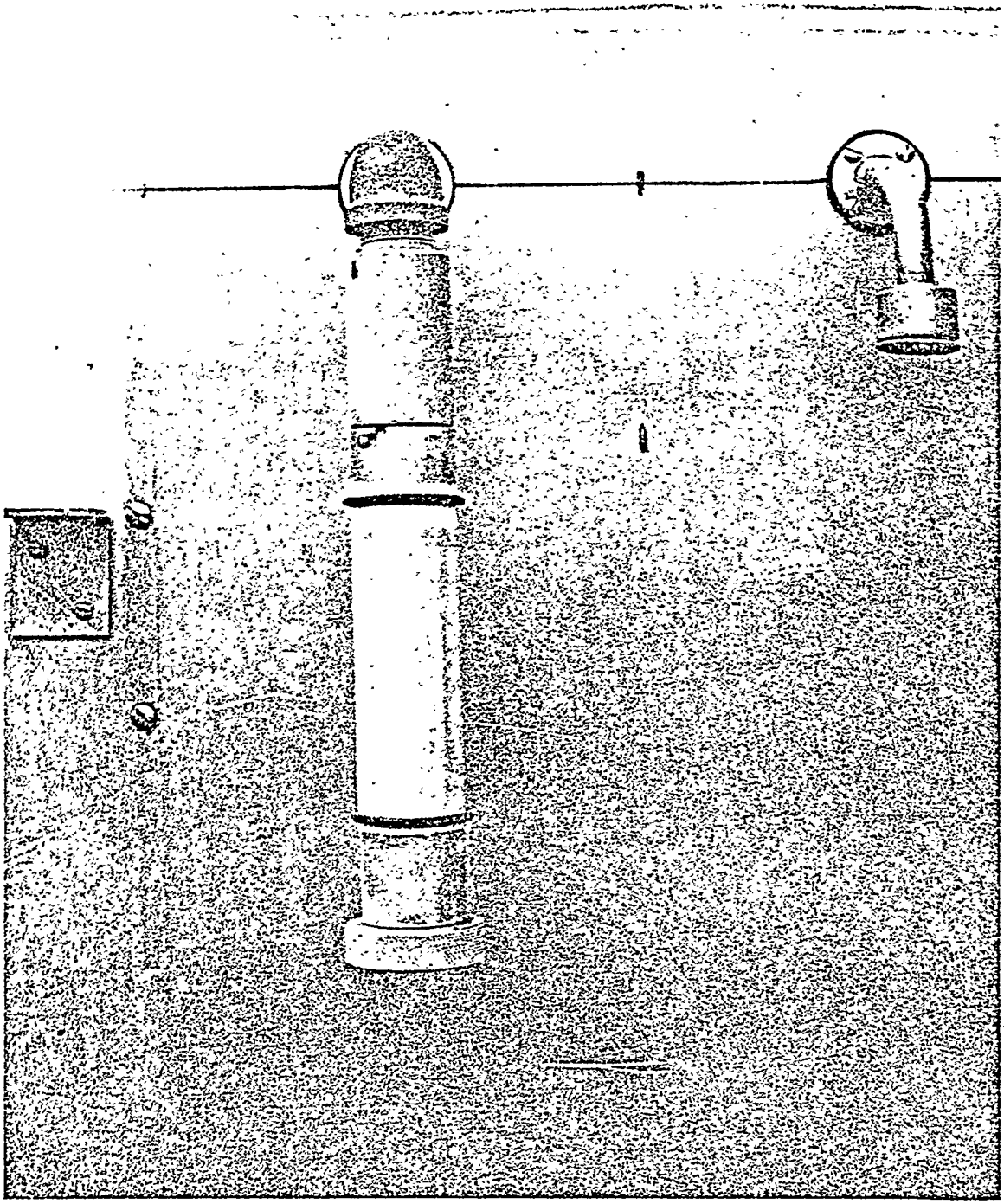

Fig. 1.1-4. A Hollingsworth and a Vose filter.

attached such that the TLDs are 1 m above the ground. Samples are exchanged monthly for the PAMs and quarterly (marked with a yellow dot), and annually (marked with a red dot) for the LAMs. Two sets of TLDs are placed at each RAM station. One set is exchanged biannually and the other set is exchanged annually. Upon completion of the predetermined exposure period, the TLDs are exchanged and returned to ORNL for reading.

Precipitation collected on the roofs of these stations flows into a 26.0-liter polyethylene jug; an overflow jug is available if needed. At the time of sample pick-up, (normally weekly), a 1-liter sample is collected from the jug after the sediment has been resuspended. The sample is labeled with the station number, date, and height of water in the jug (sample height is measured before the sample is taken). If there is water in the overflow jug, 500 ml of water is collected from each jug for a composite sample. After taking the sample, the jug is emptied and reconnected to the station. The jugs are cleaned three times yearly. During the winter, a heat lamp is focused on the jug to prevent the water from freezing. Only LAM stations 7 and 23 have provisions for water sampling; all PAM and RAM stations have this capability.

Air samples are taken by taping the Hollingsworth and Vose LB-5211 filter paper (12.5 by 12.5 cm) to the sampling tube (Fig. 1.1-4). Two O-rings help hold the filter around the tube. Air flows through the tube at a flow rate of 0.14 m^3/min (5 cfm) or less, as indicated by the flowmeter. The filter is removed, folded in half with the contaminated side inward, and placed in its respective envelope. The initial and final dates, time on and off, flow rate, and other data are recorded on the Environmental Data Card (see Appendix). Similar information is recorded on the Collection Cards (see Appendix) for all samples.

The recorded time on and off should be to the nearest hour (Table 1.1-1). A new Environmental Data Card should be left at the station. A noncontaminated Hollingsworth and Vose LB-5211 filter should be placed around the sample tube, and a new charcoal cannister should be placed in the vacuum intake line.

Table 1.1-1. Method for recording time on the Environmental Data Card

Actual time	Recorded time (nearest hour)
9:31 to 10:30 AM	10
10:31 to 11:30 AM	11
12:31 to 1:30 PM	13

The 12.5- by 12.5-cm filter paper, gummed fallout paper, water, and charcoal filter samples are exchanged weekly at PAM and LAM stations. Schedule of sampling for RAM stations will be discussed under LAM station description.

All equipment related to sampling must function properly. The air pump belt, pump oil, heat lamp, G-M detector, ratemeter, tubing, and power cords should be checked regularly.

1.2 Sample Collection at Perimeter Air Monitoring (PAM) Stations

The PAM stations are less complex than the previously described LAM stations (Fig. 1.2-1). The PAM stations do not include a moving filter or a moving fallout monitor. They do have a G-M detector to monitor the Vose LB-5211 particulate filter. The data from the Vose LB-5211 is telemetered to the CM panel board. All of the PAM stations contain facilities for collecting rainwater. The schedule of sampling at the PAM stations has already been given under the LAM stations' description; the servicing of the PAM monitoring facilities such as water, gummed fallout paper, charcoal filter, and Vose LB-5211 filter is the same as described for the LAMs.

Fig. 1.2-1. A PAM station.

1.3 Sample Collection at Remote Air Monitoring (RAM) Stations

Remote air monitoring (RAM) stations are similar to PAM stations for the types of samples collected. These stations are located remotely from ORNL so that background (control) samples can be obtained for comparison. There are seven RAM stations. Most of these are located at dam sites where TVA personnel collect the samples for ORNL. The samples are mailed to ORNL on a weekly basis. The samples are the same as those taken at PAM stations with the following exceptions:

1. The atmospheric beta-gamma activities are recorded continuously on a strip chart by the Rustrak Recorder (attached to the count ratemeter).
2. Two sets of TLDs are placed at each station. They are exchanged annually and biannually.

Because the RAM stations are located away from ORNL, each station is equipped with a materials supply box (Table 1.3-1). The RAM stations are serviced and the supply box is restocked every ten weeks. At least one RAM station is inspected biweekly.

The procedure for the collection and preparation of samples to be mailed to ORNL is available at each station. If any problems arise at the stations during the normal operating hours, TVA personnel notify ORNL.

Maintenance of the RAM stations is similar to that for the LAM and PAM stations. The charts containing the beta-gamma atmospheric activities are exchanged and returned to ORNL for evaluation. Routing procedures for the weekly collection of samples at the LAM, PAM, and RAM stations are presented in Sects. 1.4 through 1.7.

Table 1.3-1. Supply box inventory for remote air monitoring stations

Item	Quantity	Remarks
Large mailing envelopes (prestamped)	15	For gummed fallout paper
Small mailing envelopes with specific Environmental Data Card	15	For 12.5- by 12.5-cm filter paper
Hollingsworth and Vose LB-5211 filter paper (12.5 by 12.5 cm)	25	Air sampling
Gummed fallout paper	25	Particle sampling
Masking tape (1.9 cm)	1	Secures filter in place
Plastic wrap	1	Covers the gummed fallout paper samples before mailing
Mailing cannister	15	For sending water samples (precipitation)
Plastic bottles (135 ml)	15	For collecting water samples (precipitation)
Heat lamps	2	Prevent freezing of water samples
Ruler (0.45 m)	1	Measure water level in collection jug
Pump belt	1	Maintenance
Knife	1	For cutting the gummed fallout paper sample from its frame

1.4 Routing Procedures for the Local Air Monitoring (LAM) Stations

A total of 23 local air monitoring (LAM) stations are located throughout the ORNL area to monitor environmental pollutants. Thirteen LAM stations are serviced weekly; these include stations Nos. 1 through 10, 12, 16, and 20. Information from the other LAM stations (Nos. 11, 13 through 15, 17 through 19, 21, and 22) is telemetered to ORNL, but samples are not collected from these stations. Telecommunication, electrical, and other maintenance needs are handled by employees outside the Department of Environmental Management. A map of the LAM network is provided in Figs. 1.4-1 and 1.4-2.

Charcoal, air filter, and gummed paper samples are collected at most stations. Water samples are collected at LAM Nos. 7 and 23. The charcoal, air filter, and gummed paper are replaced weekly; and the excess water remaining in the bottle after the sample has been taken is discarded. TLDs are collected biannually. The date and time are recorded on an Environmental Data Card and Collection Cards (see Appendix) provided at each station.

The following materials are needed for the completion of runs: Environmental Data Cards and envelopes, Collection Cards, charcoal cannisters, gummed papers, air filters, and a 1-liter water bottle. New TLDs [TLD-100s, 0.32- x 0.32- x 0.09-cm (1/8- x 1/8- x 0.035-in.)] are needed for the biannual collection of TLDs.

The major route for all LAM stations (except Nos. 7, 8, 9, and 20) is as follows: Proceed east on White Oak Avenue from Central Research Building (Bldg. 4500), turn left onto Sixth Avenue and left onto Central Avenue.

1. LAM No. 1. Station No. 1 is located in the 3000 area and can be reached by making a left turn from Central Avenue onto Fifth Street. Proceed on Fifth Street and turn right onto White Oak Avenue. LAM station No. 1 is located to the right, in front of Bldg. 3502. The air filter and gummed paper samples are collected.
2. LAM Nos. 2 and 6. Station No. 2 is situated near the Solid State Building (Bldg. 3025) and can be reached by making a right turn

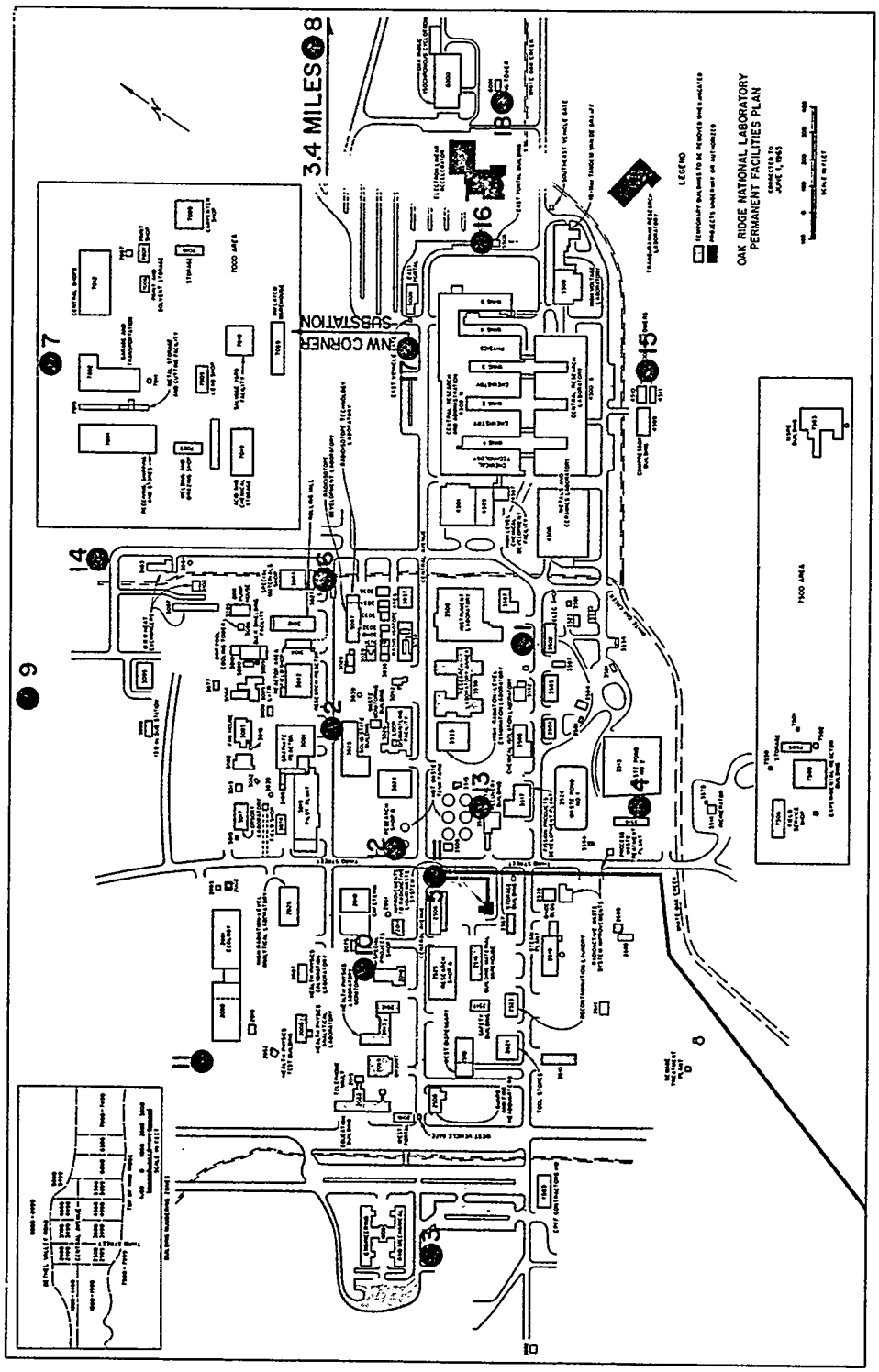

Fig. 1.4-1. Map of the local LAM stations.

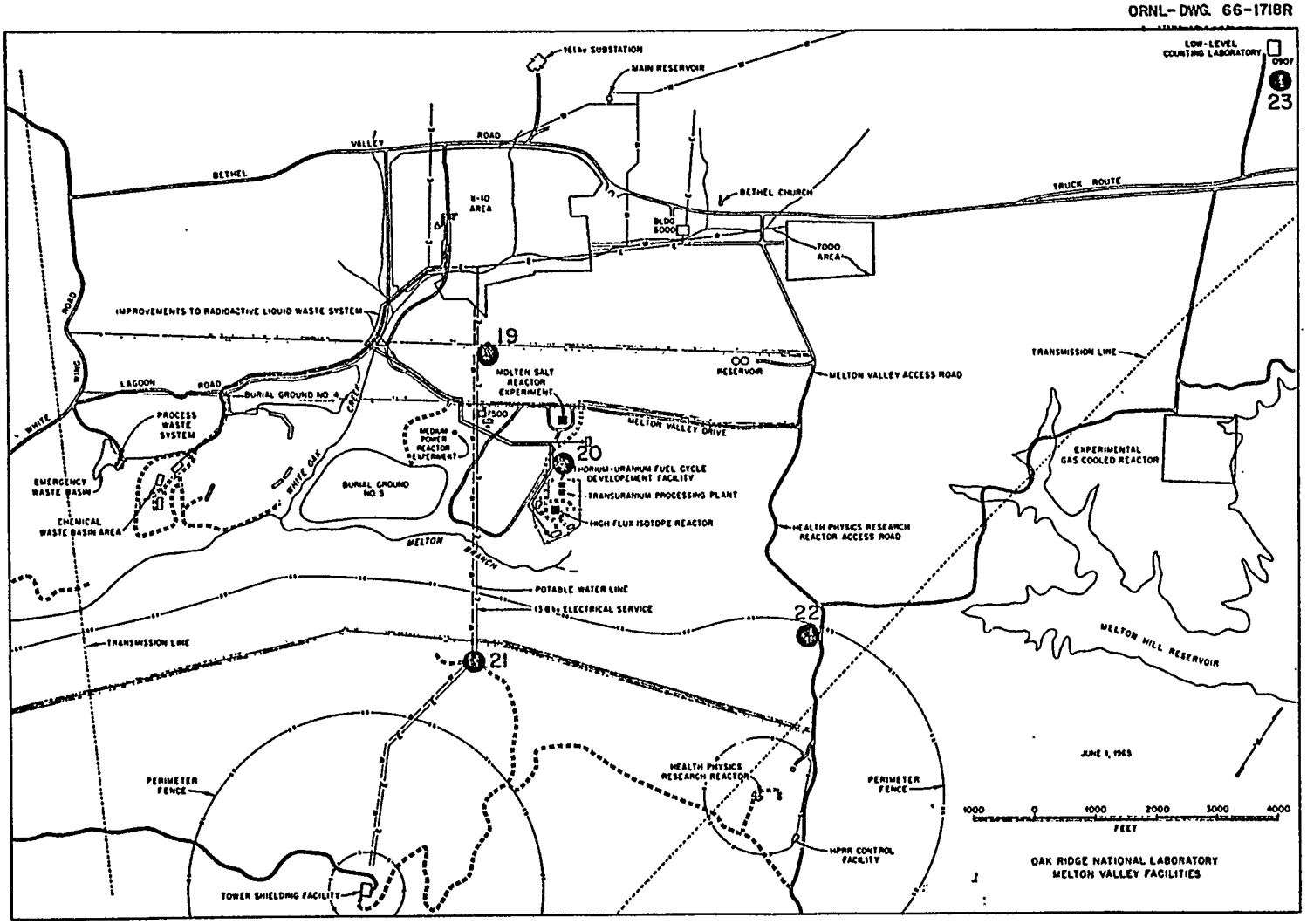

Fig. 1.4-2. Map of the local LAM stations (continued).

from Central Avenue onto Fifth Street. Proceed on Fifth Street and turn left onto Hillside. LAM Station No. 2 is at the top of the hill. LAM Station No. 6 is located at the bottom of the hill near Bldgs. 3047, 3106, and 3127. Only the air filter and gummed paper are collected at LAM Station No. 2. The gummed paper, charcoal, and air filter are collected at LAM Station No. 6.

3. LAM No. 3. Station No. 3 is located within Gate 2-B south of the Engineering Building (Bldg. 1000). Proceed on Central Avenue through the West Vehicle Gate, turn right outside the gate and left onto Westend Circle. Once inside Gate 2-B, LAM Station No. 3 can be found south of Bldg. 1000. The charcoal, air filter, and gummed paper samples are collected.

4. LAM No. 4. Station No. 4 is located near Waste Pond No. 2 (No. 3513 on map). Turn left from Central Avenue onto Third Street. Turn left just prior to Process Waste Treatment Building (Bldg. 3518). The LAM Station No. 4 is behind Bldg. 3518 near the pond. The air filter, gummed paper, and charcoal samples are collected.

5. LAM No. 5. Turn left from Central Avenue onto Third Street. LAM station No. 5 is located on the right, directly in front of Bldg. 2506. Only the air filter and gummed paper are collected.

6. LAM No. 7. Proceed east on White Oak Avenue through the 7000 area security portal. Turn left by Bldg. 7002. LAM station No. 7 is behind Bldg. 7002. Water, air filter, gummed paper, and charcoal samples are taken.

7. LAM No. 8. Proceed on White Oak Avenue through the East Vehicle Gate. Turn left onto Melton Valley Access Road and right onto Bethel Valley Road. Pass by Walker Branch Watershed Road on the left. LAM station No. 8 is approximately 5.5 km (3.4 miles) from ORNL on the right. (The rock quarry is on the left.) The charcoal, air filter, and gummed paper samples are collected.

8. LAM No. 9. Station No. 9 is on North Bethel Valley Road. From the main portal, turn left onto Bethel Valley Road. After approximately 0.8 km (0.5 mile), in front of the Graphite Reactor sign, turn right. LAM station No. 9 is located at the edge of the woods.

9. LAM No. 10. Turn right from Central Avenue onto Second Street. Turn right at Bldg. 2010. The station is in the area behind the Cafeteria (Bldg. 2010). The charcoal, air filter, and gummed paper samples are collected.

10. LAM No. 12. Turn right from Central Avenue onto Third Street. LAM station No. 12 is located on the right, northeast of the Cafeteria (Bldg. 2010). Only the air filter is collected.

11. LAM No. 16. The LAM station No. 16 is located on Sixth Street next to the East Portal Security Guard Station (Bldg. 5506). The charcoal, air filter, and gummed paper samples are collected.

12. LAM No. 20. Station No. 20 is located in the 7900 area (HFR). Proceed east on White Oak Avenue and turn right onto Melton Valley Access Road. Turn right at the intersection and proceed on this road until a security guard portal (Post 19) can be seen on the left. Turn left at the security guard portal. The gate leading to LAM station No. 20 is approximately 0.2 to 0.3 km (0.1 to 0.2 miles) from the security guard portal on the left. Ask a security guard to open the gate. Gummed paper, air filter, and charcoal samples are collected.

13. LAM No. 23. Proceed east on White Oak Avenue. Turn left onto Melton Valley Access Road. Turn right onto Bethel Valley and travel approximately 3.5 km (2.2 miles). Turn left at the Walker Branch Watershed sign. Turn right after 1.3 km (0.8 miles) onto Jim Diggs Road. Turn right onto Rain Gauge Road No. 5 and travel for approximately 1 km (0.6 mile). The distance from Bethel Valley Road to LAM station No. 23 is approximately 2.4 km (1.5 miles).

1.5 Routing Procedures for the Perimeter Air Monitoring (PAM) Stations

Nine perimeter air monitoring (PAM) stations are serviced weekly. These include No. 31 — Kerr Hollow, No. 32 — Midway, No. 33 — Gallaher, No. 34 — White Oak Dam, No. 35 — Blair, No. 36 — Oak Ridge Turnpike, No. 37 — Hickory Creek, No. 38 — Experimental Gas-Cooled Reactor (EGCR), and No. 39 — Townsite (Fig. 1.5-1). Charcoal cannister, air filter, gummed paper, and water (collected rainwater) samples are collected from each station. The charcoal cannister, air filter, and gummed paper are replaced and the excess water remaining in the container is discarded. Air flow, time on and off, and other data at each station are accurately recorded. Environmental Data Cards and envelopes, Collection Cards (see Appendix) charcoals, gummed papers, air filters, and 1-liter water bottles are needed for the completion of the run. Two uncontaminated 26-liter water jugs are needed for water samples to be taken at Melton Hill Dam and Gallaher. Thermoluminescent dosimeters (TLDs) [TLD-200, 0.64- x 0.64- x 0.089-cm (0.25- x 0.25- x 0.035-in.)] are exchanged monthly.

1. PAM No. 31 — Kerr Hollow. Proceed east on White Oak Avenue. Turn left onto Melton Valley Access Road and right onto Bethel Valley Road. Continue past the Comparative Animal Research Laboratory (CARL), which is approximately 10.5 km (6.5 miles) from ORNL. The PAM station No. 31 is on the left behind the white security guard portal, approximately 0.3 km (0.2 mile) from CARL.

2. PAM No. 32 — Midway. Proceed east on White Oak Avenue. Turn left onto Melton Valley Access Road and right onto Bethel Valley Road. Proceed east on Bethel Valley Road. Turn left at the Y-intersection. Proceed on this road for approximately 3.9 km (2.4 miles). The PAM station No. 32 is located behind the white security portal on the right.

3. PAM No. 33 — Gallaher. Proceed on White Oak Avenue through East Vehicle Gate. Turn left and go through parking lot. Turn left onto Bethel Valley Road and proceed for approximately 3.2 km (2 miles). At the intersection of Highway 95 and Bethel Valley

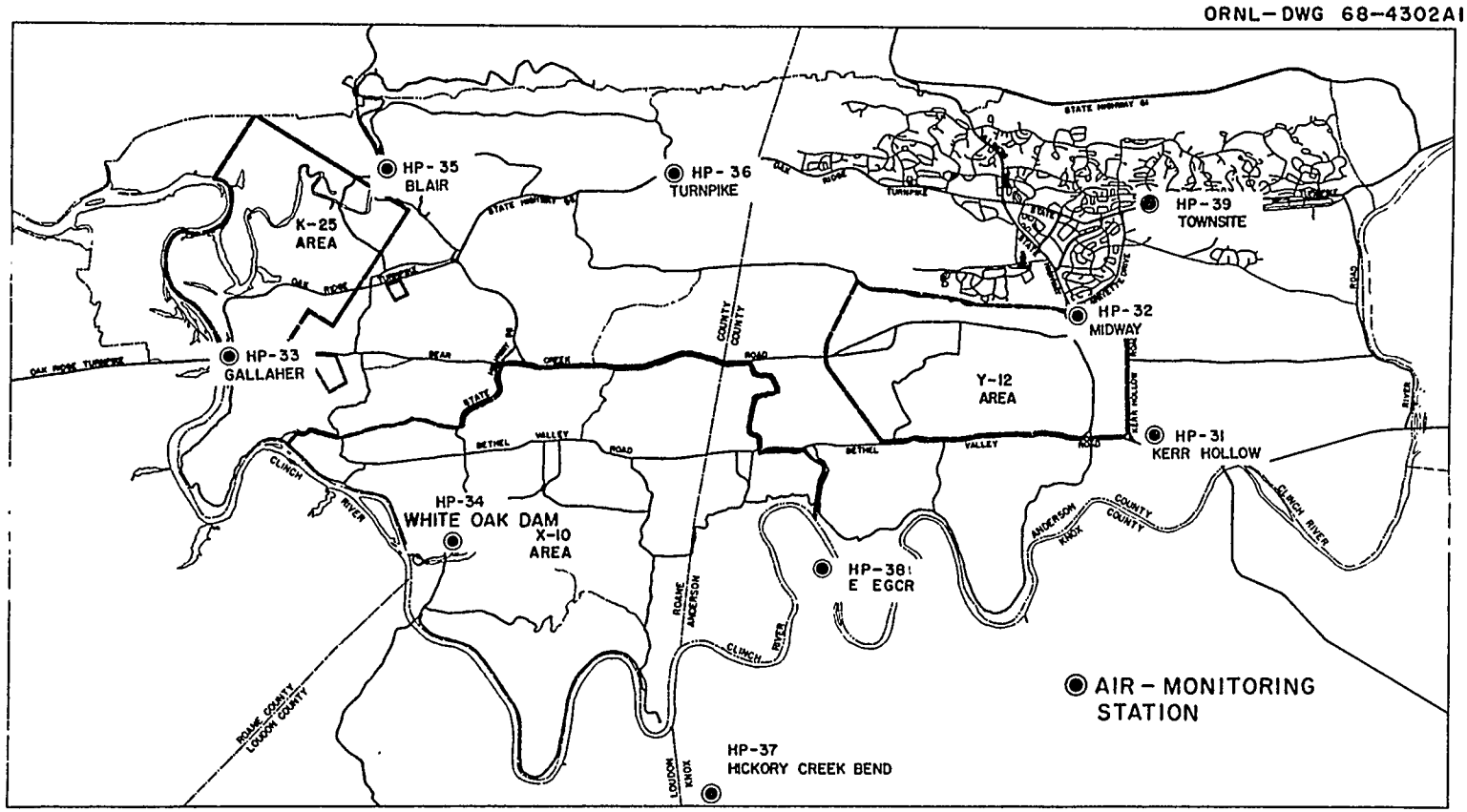

Fig. 1.5-1. Map of the Perimeter Air Monitoring (PAM) Stations.

Road, turn right. Proceed approximately 2.4 km (1.5 miles) to Bear Creek Road. Turn left onto Bear Creek Road. The PAM station No. 33 is on Bear Creek Road beside the Clinch River approximately 5.6 km (3.5 miles) from the intersection of Bear Creek Road and Highway 95. For information on the Gallaher Water Sampling Station, see Water Sampling Section, Sect. 4.

4. PAM No. 34 — White Oak Dam. Proceed east on White Oak Avenue through East Vehicle Gate. Turn left and go through parking lot. Turn left on Bethel Valley Road and proceed for approximately 3.2 km (2 miles). Turn left at the intersection of Bethel Valley Road and Highway 95. Proceed for approximately 2.4 km (1.5 miles). The PAM No. 34 is on the left before White Oak Dam.

5. PAM No. 35 — Blair. Proceed east on White Oak Avenue through East Vehicle Gate. Turn left and go through parking lot. Turn left onto Bethel Valley Road and proceed for approximately 3.2 km (2 miles). Turn right onto Highway 95 and proceed approximately 5.3 km (3.3 miles). Turn left onto Highway 58 and travel approximately 1.4 km (0.9 miles). Turn right onto Blair Road, cross single-lane bridge, and proceed for approximately 3.5 km (2.2 miles). The PAM No. 35 is on the left by the white security guard portal.

6. PAM No. 36 — Oak Ridge Turnpike. Proceed east on White Oak Avenue. Turn left onto Melton Valley Access Road. Turn left onto Bethel Valley Road and proceed for approximately 3.2 km (2 miles). Turn right onto Highway 95 and proceed to the intersection of Highways 95 and 58. Turn right onto Highway 58 toward Oak Ridge. Travel approximately 4.8 km (3 miles) to the point where Highway 58 becomes a four-lane highway. PAM station No. 36 is on the right, next to the security guard portal.

7. Pam No. 37 — Hickory Creek. Proceed east on White Oak Avenue through East Vehicle Gate. Turn left and go through parking lot. Turn left onto Bethel Valley Road and proceed approximately 3.2 km (2 miles). Turn left onto Highway 95 and proceed for approximately 5.1 km (3.2 miles). Turn left onto I-40 and proceed toward Knoxville.

Exit at Watt Road (Exit 369). Turn left onto Watt Road and proceed approximately 2.1 km (1.3 miles). Turn right onto Buttermilk Road and then to the immediate left by Gerald Smith's mailbox. PAM No. 37 is between the mailbox and house.

8. PAM No. 38 — Experimental Gas-Cooled Reactor (EGCR). Proceed east on White Oak Avenue through East Vehicle Gate. Turn left and go through parking lot. Turn left onto Bethel Valley Road and proceed approximately 3.2 km (2 miles). Turn left onto Highway 95 and proceed for approximately 5.1 km (3.2 miles). Turn left onto I-40 and proceed toward Knoxville. Exit at Watt Road, Exit 369. Turn left onto Watt Road and proceed approximately 2.1 km (1.3 miles). Turn right onto Buttermilk Road. Proceed 0.2 km (0.1 mile). Turn left onto Hickory Creek Road. Proceed approximately 3.5 km (2.2 miles). Turn left onto Gallaher Ferry Drive. Proceed approximately 5.1 km (3.2 miles). The PAM station No. 38 is located on the left at the end of the road directly across Melton Hill Lake from the Experimental Gas-Cooled Reactor.

9. PAM No. 39 — Townsite. Proceed east on White Oak Avenue. Turn left onto Melton Valley Access Road and right onto Bethel Valley Road. Proceed for approximately 10.4 km (6.5 miles). Turn left at the Y-intersection onto Scarboro Road. Proceed for approximately 4 km (2.5 miles). Turn right at the Y-intersection onto Lafayette Drive. Travel approximately 2.4 km (1.5 miles). Turn right onto the Oak Ridge Turnpike. Travel approximately 0.6 km (0.4 mile). Turn left into Doctor's Building parking lot. The PAM No. 39 is located on the north end of the parking lot, across from French's Plaza.

10. Melton Hill Dam Water Sample. Normally, the Melton Hill Dam water sample is collected during the PAM sample collection. For information, see Water Sampling Section, Sect. 4.

1.6 Routing Procedures for Servicing Local and Perimeter Air Monitoring (LAM and PAM) Stations

This section gives the procedures normally followed in servicing the LAM and PAM stations. They are combined for greater efficiency.

1. Materials Needed for Route
   - 1.1 New charcoal cartridges
   - 1.2 Gum papers
   - 1.3 Air filter papers (12.5- by 12.5-cm Hollingsworth and Vose-5211)
   - 1.4 Eleven 1-liter plastic bottles for water collection
   - 1.5 Envelope and Computer Card (see Appendix)
   - 1.6 Maps of ORNL and Tennessee
   - 1.7 Keys (3F16 and 3D7)
   - 1.8 26-liter water jugs: one for Melton Hill and one for Gallaher (K-25 water station)
   - 1.9 Charts for instruments at Gallaher and Melton Hill

2. Code
   - CC — Charcoal cartridge
   - AF — Air filter
   - GP — Gummed fallout collection paper
   - W — Water sample
   - LAM — Local air monitor
   - PAM — Perimeter air monitor

3. Preparation
   - 3.1 On the day before servicing LAMs and PAMs (e.g., Friday for a Monday run), prepare computer cards for each PAM and LAM.
   - 3.2 Prepare all materials necessary for routing procedure (see step 1 of this procedure).

4. Routing Procedure
   - 4.1 LAM No. 16. Proceed on White Oak Avenue and turn left onto Sixth Street. LAM No. 16 is located on the right, by the East Security Portal. Perform CC, AF, and GP (see step 2 of this procedure).

4.2 LAM No. 6. From LAM No. 16, proceed on Sixth Street to Central Avenue. Drive by the main portal. Turn right on Fifth Street and left at the Storage Vault Building (the street is not marked). Continue on this street until Bldg. 3047 (Radioisotope Development Laboratory) can be seen on the left. LAM No. 6 is in front of Bldg. 3047. (CC, AF, and GP)

4.3 LAM No. 2. After servicing LAM No. 6, continue driving on Fifth Street until Bldg. 3025 can be seen on the left. LAM No. 2 is on the left, in front of Bldg. 3025. (AF and GP)

4.4 LAM No. 12. Return to Central Avenue. Turn right and drive approximately 0.7 km (0.45 mile) to Third Street. Turn right onto Third Street. LAM No. 12 is on the right, across from the Cafeteria. (AF)

4.5 LAM No. 10. Return to Central Avenue and turn right. Drive approximately 0.2 km (0.1 mile) and turn right at Bldg. 2018 onto Second Street North. Turn right onto cafeteria service area parking lot. LAM No. 10 is located on the left side of the drive. (CC, AF, and GP)

4.6 LAM No. 5. Return to Central Avenue and turn left. Continue on Central Avenue to the intersection of Third Street and Central Avenue. Turn right onto Third Street. LAM No. 5 is located on the right, beside the Instrument Fabrication Shop and Timekeeping (Bldg. 2506). (AF and GP)

4.7 LAM No. 4. Continue driving on Third Street for approximately 0.24 km (0.15 mile). Turn left onto the drive located beside the Waste Treatment Plant. LAM No. 4 is located beside Waste Pond No. 2. (CC, AF, and GP)

4.8 LAM No. 1. Drive from Waste Treatment parking lot to White Oak Avenue. Turn right and travel approximately 0.3 km (0.2 mile) to Bldg. 3500 (Instrumentation Laboratory). LAM No. 1 is located on the left, in front of the Instrumentation Laboratory. (AF and GP)

4.9 Return to ORNL parking lot. Turn left onto Fifth Street and drive to the intersection of Fifth Street and Central Avenue. Turn right onto Central Avenue and right onto Sixth Street. Turn right at White Oak Avenue to parking lot.

4.10 PAM No. 33. Before leaving ORNL, call Tim Bard, K-25 Environmental Management Group (4-8223). He will unlock the gate to Gallaher Water Collection Station and the door to the pumping station building. Drive from ORNL parking lot on White Oak Avenue and turn left onto Sixth Street; continue to the West Portal. Proceed through the gate and turn right. Continue for approximately 0.2 km (0.1 mile) and turn left onto Bethel Valley Road. Drive approximately 3.2 km (2 miles) on Bethel Valley Road to the intersection of Highway 95. Turn right onto Highway 95 and continue to Bear Creek Road. Turn left onto Bear Creek Road. PAM No. 33 is approximately 5.6 km (3.5 miles) from the intersection of Bear Creek Road and Highway 95. Turn left onto drive of Gallaher Water Sampling station. PAM No. 33 is located approximately 15.2 m (50 ft) to the right of the gate. (CC, AF, GP, and W)

4.11 Gallaher Water Sampling Station (GWSS). See Water Sampling Section, Sect. 4.

4.12 PAM No. 35 — Blair. Return to Bear Creek Road and turn left. Drive under Highway 58 bridge until you come to a three-road intersection. Take the middle road, which will circle around to Highway 58. Turn left onto Highway 58. Travel 1.6 km (1 mile), by-passing K-25, to Blair Road. Turn left onto Blair Road and continue over a single-lane bridge. After crossing railroad tracks, PAM No. 35 is located approximately 0.2 km (0.1 mile) on the left, beside the white security guard portal. (CC, AF, GP, and W)

4.13 PAM No. 36 — Oak Ridge Turnpike-Highway 95. Return to Highway 58 and turn left. Proceed 0.2 km (0.1 mile) and turn left onto Highway 58/95N. Before the highway becomes

four-lane, PAM No. 36 will be on the right, beside a white security guard portal. (CC, AF, GP, and W)

4.14 PAM No. 39 — Townsite. Continue driving east on Highway 95 (Oak Ridge Turnpike) to the business district. PAM No. 39 is located on the left of Highway 95 across from French's Plaza. Turn left onto parking lot of the Doctor's Building. PAM No. 39 is located on the north end of this parking lot. (Property on which PAM No. 39 is located is the UCCND Post Office Facility.) (CC, AF, GP, and W)

4.15 PAM No. 32 — Midway. From Doctor's Building parking lot, turn right onto Highway 95S and left at Lafayette Avenue. Drive to the intersection of Lafayette and Illinois Avenues (Highway 62). Continue through intersection and veer left onto Scarboro Road. White security guard portals are less than 0.2 km (0.1 mile) from the intersection. PAM No. 32 is located on the left, behind the security guard portal. (CC, AF, GP, and W)

4.16 PAM No. 31 — Kerr Hollow. Continue on Scarboro Road to Bethel Valley Road (veer left at the Y-intersection). Turn left at the intersection of Bethel Valley and Scarboro Road. PAM No. 32 is located on the left, behind the white security guard portal (diagonal to Comparative Animal Research Laboratory — CARL). (CC, AF, GP, and W)

4.17 LAM No. 8 — Rock Quarry. Proceed south on Bethel Valley Road toward ORNL. LAM No. 8 is located on the left approximately 5.6 km (3.7 miles) from PAM No. 31 (across from the rock quarry). (CC, AF, and GP)

4.18 PAM No. 23 — Walker Branch. Continue traveling on Bethel Valley Road toward ORNL for 3.2 km (2.0 miles) and turn right onto Walker Branch Road. (Use key 3F16 to open the gate.) Continue on Walker Branch Road to Jim Diggs Road [approximately 1.4 km (0.9 mile) from Bethel Valley Road]. Turn right onto Jim Diggs Road and right onto Rain Gauge Road No. 5. Travel for approximately 1.1 km (0.7 mile) to PAM No. 23. (CC, AF, GP, and W)

4.19 LAM No. 9 — North Bethel Valley. Return to Bethel Valley Road after locking gate to Walker Branch Road. Turn right onto Bethel Valley Road. LAM No. 9 is located on the right after by-passing the Graphite Reactor. The station is approximately 27.4 m (30 yd) from the road, across from Building 3017. (CC, AF, and GP)

4.20 LAM No. 3 — SW Bldg. 1000. Turn right onto Bethel Valley Road. Travel approximately 0.2 km (0.1 mile) and turn left toward the West Portal area (1000 area). Turn right onto Westend Circle and proceed around the north side of the Engineering Building (1000). Enter the fenced area at the rear of the building. LAM No. 3 is located on the south side of Bldg. 1000 (see Fig. 1.6). (CC, AF, and GP)

4.21 Return to ORNL (for lunch). Drive to the West Portal. Travel through portal on Central Avenue to Sixth Avenue, and continue on Sixth Street to White Oak Avenue. Turn right on White Oak Avenue and proceed to parking lot.

4.22 PAM No. 34 — White Oak Dam (WOD). Proceed from ORNL parking lot on White Oak Avenue. Turn left onto Sixth Street and continue on Sixth Street to Central Avenue through the West Gate. Turn left onto Lagoon Road. At intersection of Lagoon Road and Highway 95, turn left. PAM No. 34 is located on the left before White Oak Dam. (CC, AF, GP, and W)

4.23 PAM No. 37 — Hickory Creek. Continue south from PAM No. 34 on Highway 95 past Melton Hill Dam and turn left onto I-40 East. Continue driving on I-40 East to the Watt Road Exit. Exit and turn left onto Watt Road (also called Everett Road). Proceed on Watt Road for 1.6 km (1 mile). Turn right onto Buttermilk Drive and to the immediate left onto the driveway. PAM No. 37 is located on the right. (CC, AF, GP, and W)

4.24 PAM No. 38 — EGCR. Turn left onto Buttermilk Road from driveway and left onto Hickory Creek Road. Travel Hickory Creek Road for approximately 3.7 km (2.3 miles) to Gallaher Ferry Road. Turn left on Gallaher Ferry Road and drive

approximately 4.9 km (3.1 miles) to PAM No. 38, located on the left. (CC, AF, GP, and W)

4.25 Melton Hill Water Sampling Station (MHWSS). See Water Sampling Section, Sect. 4.

4.26 LAM No. 20. Lock gate to MHWSS and return to Highway 95. Turn right onto Highway 95 North and travel approximately 5.3 km (3.3 miles) to Lagoon Road. Turn right onto Lagoon Road. Travel Lagoon Road to Melton Valley Drive (crossing White Oak Creek). Turn right onto Melton Valley Drive and continue driving for 1.6 km (1 mile) to 7900 guard gate (Post 19). Turn right at gate. Call KIN-294 when leaving MHWSS and ask them to unlock the first gate on the left inside Post 19. (CC, AF, and GP)

4.27 LAM No. 7. Return to Post 19 guard gate and turn right onto Melton Valley Road. Travel approximately 1.6 km (1 mile) to the intersection of Melton Valley Access Road and White Oak Avenue. Turn right onto White Oak Avenue and drive through 7000 Guard Gate to Garage and Transportation Complex (Bldg. 7022). LAM No. 7 is located inside the fence behind the garage building (north side W, CC, AF, and GP).

4.28 Return to ORNL parking lot. Turn right from Garage Complex onto White Oak Avenue. Continue through East Gate to ORNL parking lot.

1.7 Routing Procedures for the Remote Air Monitoring (RAM) Stations

Routing procedures have been developed for the servicing of RAM stations (Fig. 1.7-1). When servicing RAM stations located inside switch yards at dams, the dam supervisors are to be notified. The supervisors, who are usually inside the control rooms, will unlock and lock the gates to the switch yards before and after inspections of the RAM stations. Hard hats must be worn inside switch yards, and the supply box (in the control room) must be restocked before leaving the station.

One or two RAM stations are serviced weekly in conjunction with the collection of the remote milk samples. The air filters, gummed papers, and water samples are collected weekly from the RAM station by TVA or Corps of Engineers onsite personnel.

1. RAM No. 51 — Norris Dam. Proceed east on White Oak Avenue. Turn left onto Melton Valley Access Road. Turn right onto Bethel Valley Road and proceed east. Turn right onto Edgemoor Road. Cross Clinton Highway (Highway 25 West) and continue on Raccoon Valley Road. Follow Raccoon Valley Road to the Interstate-75 intersection. Turn onto Interstate-75 and drive approximately 4.8 km (3 miles) and exit at the Clinton/Norris exit. Turn right onto old Highway 61 and continue to Norris Dam.

2. RAM No. 52 — Loudon Dam. Proceed east on White Oak Avenue. Turn left onto Sixth Street/Central Avenue and continue through West Gate. Turn left onto Lagoon Road. Proceed to Highway 95. Turn left onto Highway 95. Proceed approximately 24.1 km (15 miles). Cross Highway 11. Proceed 0.16 km (0.1 miles) and turn right onto Loudon Dam Drive. To go to control room, turn left at the first Y-intersection and right at the second Y-intersection. The supervisor who is responsible for opening the gate will ride with ORNL personnel to the switch yard. To go to the switch yard, return to the last intersection and turn right. Proceed 0.16 km (0.1 mile) and turn right again.

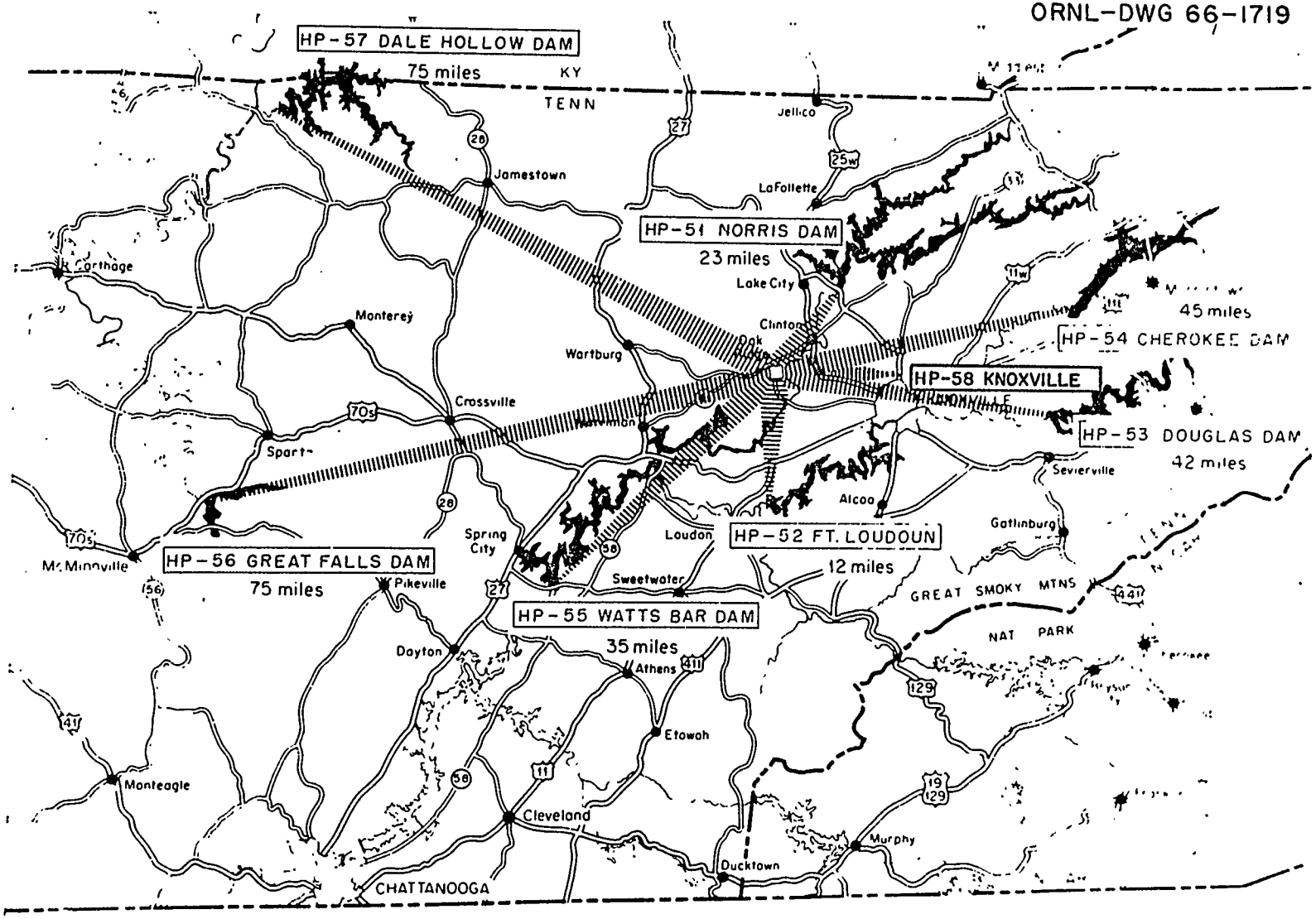

Fig. 1.7-1. Map of remote air monitoring stations.

3. RAM No. 53 — Douglas Dam. Proceed east on White Oak Avenue. Turn left onto Melton Valley Access Road. Turn right onto Bethel Valley Road and drive for approximately 10.5 km (6.5 miles). Cross over Solway Bridge and continue to Knoxville on Highway 162 (Pellissippi Parkway). Merge left onto Interstate-40/75. Continue through Knoxville on Interstate-40. Exit at 407/Sevierville. Turn right toward Sevierville on Highway 66 South. Proceed approximately 8 km (5 miles). Turn left onto Highway 66 East (toward Dandridge). Proceed approximately 8 km (5 miles) and turn right onto Douglas Dam Road (northside). The RAM station is inside the switch yard. The station is approximately 96.5 km (60 miles) from ORNL.

4. RAM No. 55 — Watts Bar Dam. Proceed on White Oak Avenue through East Vehicle Gate and turn left. Go through parking lot and turn left onto Bethel Valley Road. Proceed for approximately 3.2 km (2 miles). Turn right onto Highway 95. Proceed to the intersection of Highways 95 and 58. Turn left onto Highway 58 and go past the K-25 Gaseous Diffusion Plant. Turn right onto Interstate-40 to Kingston. From Kingston, proceed south on Highway 58. Turn right onto Highway 68 East. Continue on 68 East for approximately 14.5 km (9 miles). The Watts Bar Dam power house is on the left.

5. Ram No. 56 — Great Falls. Proceed on White Oak Avenue to the East Parking Lot. Drive through the parking lot and turn left onto Bethel Valley Road. Continue on Bethel Valley Road to the intersection of Highway 95 and turn right. Proceed approximately 2.3 km (1.4 miles) and turn left onto Bear Creek Road. Continue on Bear Creek Road, pass under Highway 58, and turn right onto the second road [approximaterly 6.6 km (4.1 miles)]. Turn right onto Highway 58 and proceed to Kingston. Travel approximately 6.6 km (4.1 miles) and turn right onto Interstate-40 West. Proceed approximately 54.4 km (38.8 miles) and exit at Crossville/Jamestown (Exit 317). Turn left and travel toward Crossville on Highway 127/28 South. Turn right onto Highway 70 West through Sparta, Tenn., and turn left by the Commerce Union Bank. Proceed approximately 20.6 km (12.8 miles) through Doyle and Walling. Pass Browne Cafe in Walling, turn to the immediate right, and continue

to the Rock Island State Park by following the signs. Caution should be exercised because of the narrow road and the wooden bridge. After crossing the bridge, turn right and proceed to the main office of the park. The total distance is approximately 2.1 km (1.3 miles) from Highway 70 West.

6. RAM No. 57 — Dale Hollow. When servicing RAM 57, the technician should follow the routing procedure for RAM station 56, return to Doyle, and turn left onto Highway 111 North toward Cookville (before entering Sparta). (If RAM 57 is not to be serviced, the technician should return to the Laboratory.) Proceed approximately 20.1 km (13 miles) on Highway 111 North and turn left onto Highway 42 North. Proceed approximately 4 km (2.5 miles) on Highway 42 North and turn left onto Interstate-40 West toward Nashville. Travel approximately 11.6 km (7.2 miles) toward Nashville. Travel approximately 11.6 km (7.2 miles) and exit at the Baxter/Gainesboro exit, (Exit 280, Highway 56 North). Turn right onto Highway 56 North and proceed toward Gainesboro. Instead of traveling the business district of Gainesboro, proceed toward Celina on Highway 53 North about 29.8 km (18.5 miles). Continue on Highway 53 North until a large sign for Dale Hollow Dam can be seen on the right (disregard the Celina and Dale Hollow Lake's signs before the Dam's sign). Turn right by the sign and proceed to the powerhouse 0.8 km (0.5 mile). Use the outside phone to call the operator before entering the building.

   When leaving the RAM 57, the technician should turn right at the end of the powerhouse driveway, travel approximately 1.2 km (0.7 mile) and turn right onto the Dale Hollow Lake Bridge. Continue across the bridge to Highway 52 East [4 km (2.5 miles)] and turn left. Drive about 21.7 km (13.5 miles) and turn right (toward Cookeville) on Highway 42 South. Continue on Highway 42 South for approximately 2.6 km (1.6 miles) and turn left onto Highway 84 South (Sam B. Coward Highway) toward Monterey. Drive approximately 26.9 km (16.7 miles) and turn right onto Highway 84 South. Travel approximately 0.5 km (0.3 mile) and turn left at flashing caution light onto Highway 70 East. Go approximately 0.9 km (0.6 mile) and turn left

onto Interstate-40 toward Knoxville. Exit at the Oak Ridge/Gallaher Exit (Highway 58). Turn left onto Highway 58 and travel approximately 6.6 km (4.1 miles) to Bear Creek Road. Turn right and to the immediate right onto Bear Creek Road. Proceed approximately 6.6 km (4.1 miles) and turn right onto Highway 95, proceed approximately 2.2 km (1.4 miles) and turn left onto Bethel Valley Road. Continue to the Laboratory [about 3.2 km (2 miles)].

7. RAM No. 58 — Knoxville truckpool, TVA site. Proceed east on White Oak Avenue. Turn left onto Melton Hill Access Road and right onto Bethel Valley Road. Proceed approximately 11.3 km (7 miles). Turn right onto Edgemoor Road. Turn right onto Clinton Highway (Highway 25 West). Exit at Interstate-640 and proceed to Broadway. Turn right onto Broadway and to the immediate right onto Greenway Road. Go approximately 1.6 km (1 mile) and cross railroad tracks. The facility is on the left.

1.8 Central Monitoring Station Panel

1. Introduction

The Central Monitoring Station (CMS) panel located in Building 4500S, room H-251, provides monitoring facilities for meteorological data, the local and perimeter air monitoring (LAM and PAM) stations, and White Oak Dam (WOD). Data are transmitted to the CMS by telephone lines. The CMS is shown in Fig. 1.1-2 and a detailed description and operating procedures are included in the Appendix.

Basically the CMS provides for the recording of data and has an alarm system. Data are recorded by multipoint Brown recorders, five single-point recorders and one multipoint EA recorder. The alarm system has indicator lamps, a map displaying the station location of the indicator lamps, provision for alerting guard headquarters, and a large flashing orange light for alerting a Department of Environmental Management employee.

2. Description of CMS Readout and Alarm Functions

2.1 LAMs — LAMs (1-22) air filters are monitored for beta gamma radiation. If the counts per minute (c/min) exceed 1300, the alarms are activated.

2.2 FOMs — The 22 fallout monitors (FOMs) located at the LAMs are telemetered to the CMS. Any 12 of the 44 beta-gamma or alpha c/m can be selected for monitoring by means of a patchcord panel. If one of the 12 selected FOMs has a c/min exceeding 200 c/m, the alarms are activated.

2.3 PAMs — PAMs 1-6 and 9 air filters are monitored for beta-gamma radiation; if the c/min exceed 2000, the alarms are activated.

2.4 WOD — The following data are telemetered to the CMS from White Oak Dam:

2.4.1 height of WOD above 740 feet, displayed on a digital voltmeter; above 750 activates the alarm

2.4.2 pump failure alarm

2.4.3 effluent water — beta-gamma radiation is monitored; a high level activates an alarm.

2.5 Weather information — Temperature, temperature gradient, dew point, wind direction, and wind velocity are monitored by CMS. The weather sensors are located on the roof of Building 4500S. There are no alarm signals associated with the meteorological data.

3. Data Interpretation, Operator Controls, and Operating Procedure and Reporting

3.1 Data interpretation, operator controls, and operating procedure are discussed in detail in the Appendix. This information is also posted on the right side of the CMS console.

3.2 Reporting — When an alarm has been activated, it should be considered as an emergency alert until determined otherwise.

3.3 Diagnostic diagrams in the form of flow charts (Figs. 1.8-1–1.8-3) are given in the Appendix. These will aid in ascertaining what action is required. By using the procedure given in the diagnostic aid, usually it will be possible to resolve the situation into one of the following categories.

3.3.1 The alarm was caused by some transient artifact. If after setting the alarm all appears normal, no further action is required.

3.3.2 The alarm was caused by an instrumentation malfunction and the I&C maintenance should be notified.

3.3.3 The alarm was probably due to a high radiation level and the department head should be notified (during the regular day shift) or the Radiation Survey Shift Supervisor (during any other shift). If for some reason neither individual can be contacted, someone in the Department of Environmental Management should check the situation immediately.

ORNL-DWG 80-17555

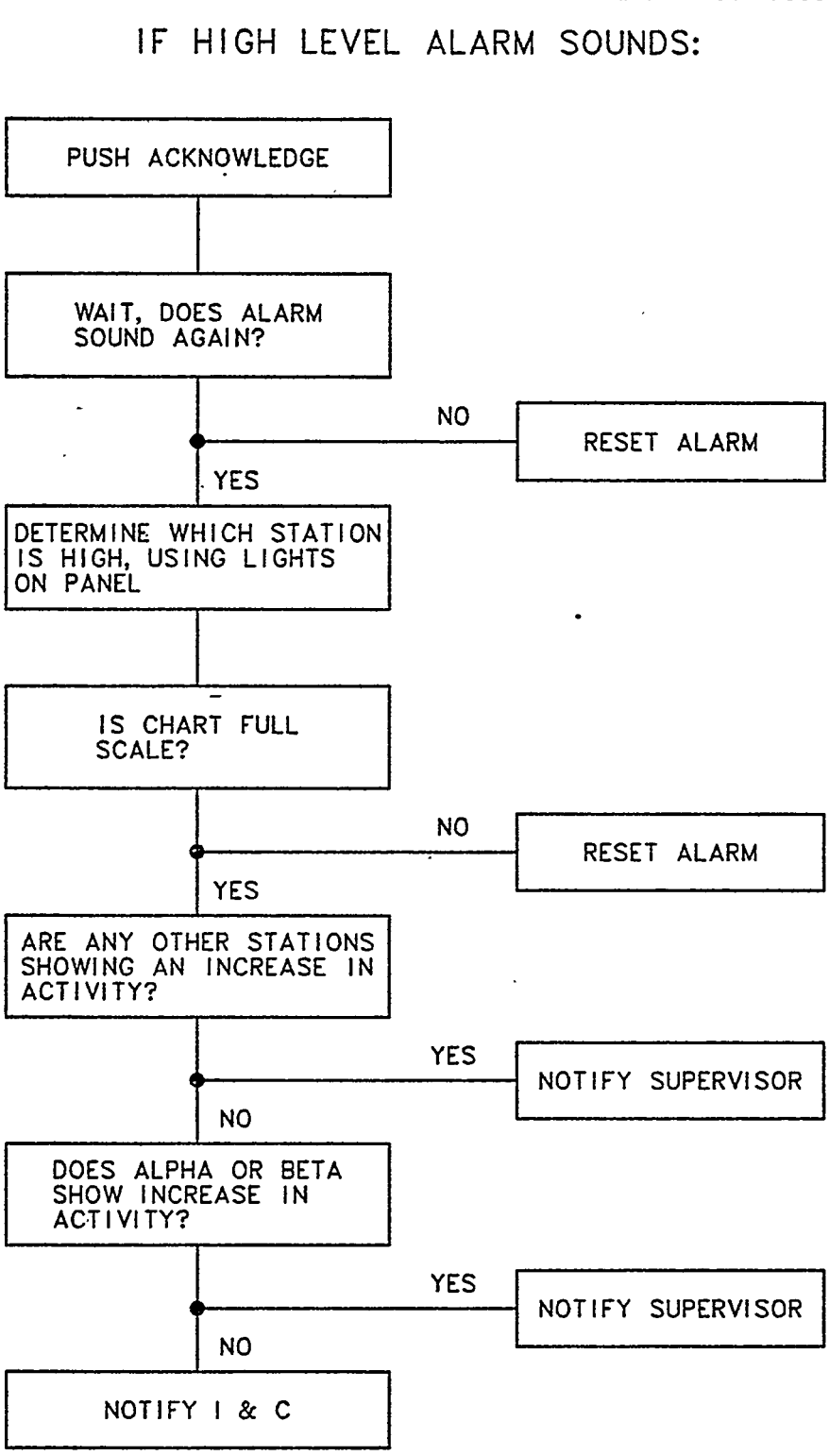

Fig. 1.8-1. Emergency reporting procedure.

ORNL-DWG 80-17553

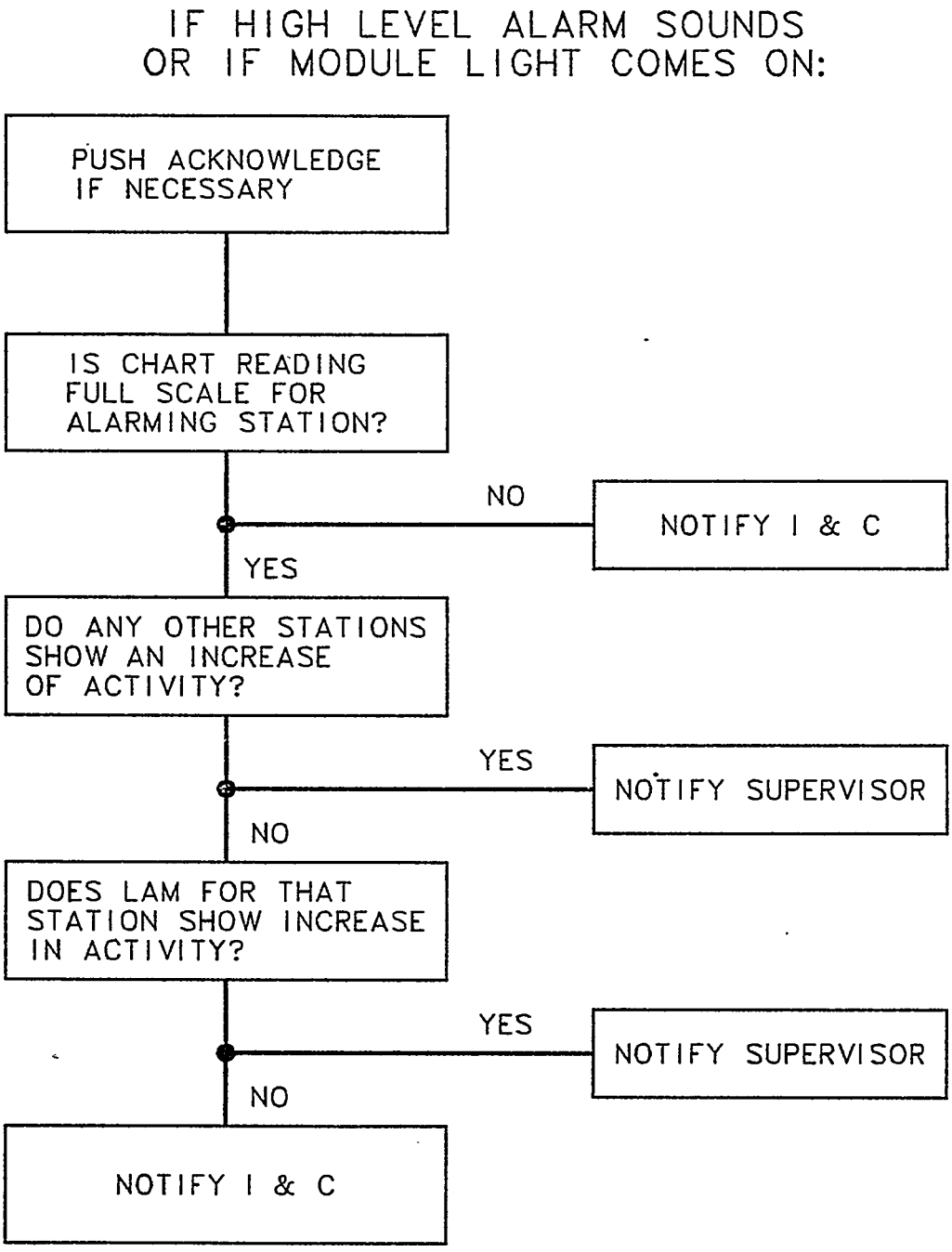

Fig. 1.8-2. Emergency reporting procedure.

ORNL-DWG 80-17554

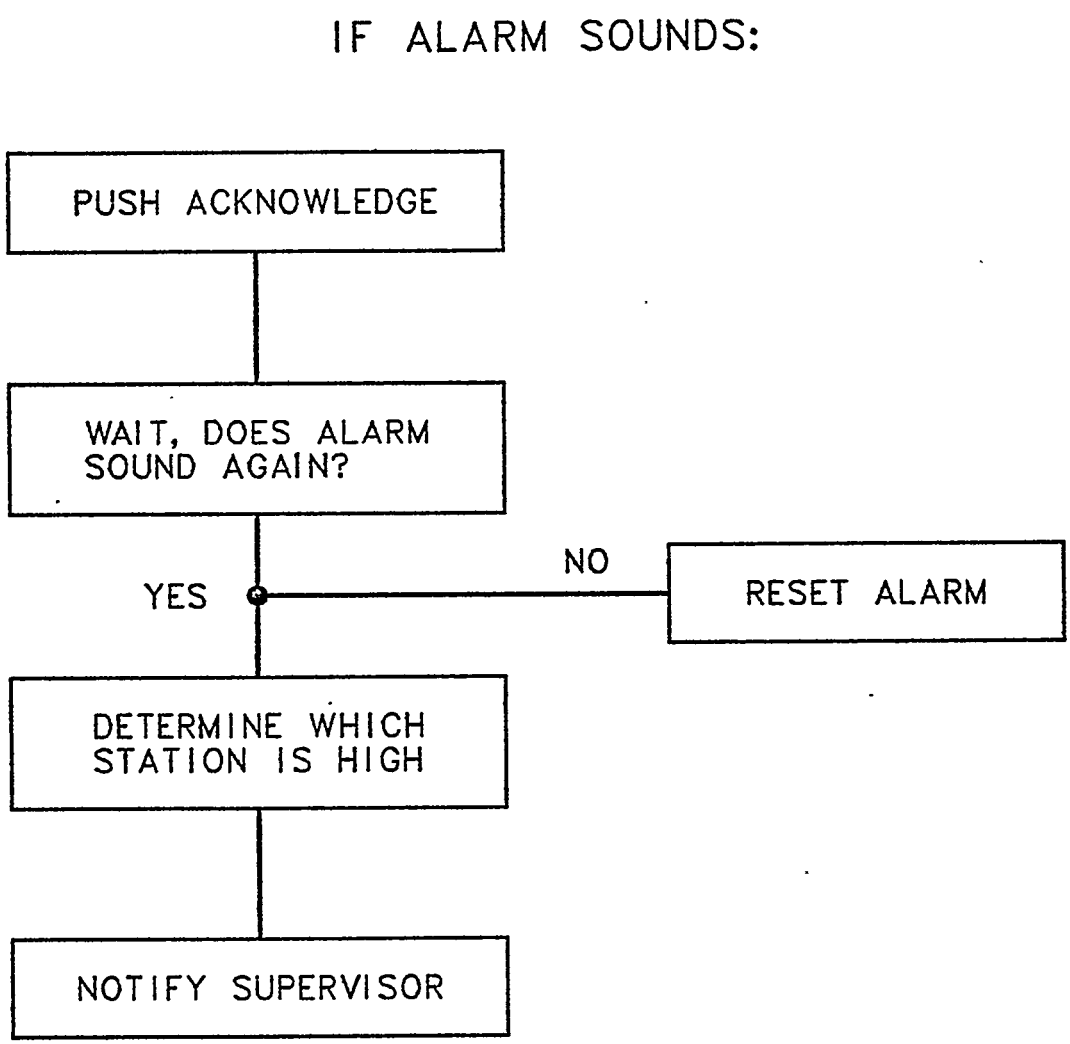

Fig. 1.8-3. Emergency reporting procedure.

1.9 Processing of Gummed Fallout Paper for the Local, Perimeter, and Remote Air Monitoring (LAM, PAM, RAM) Stations

1. LAM

The LAM gummed fallout papers (Fig. 1.9-1) are exchanged on Mondays. The routine processing of these papers for the evaluation of radioactivity begins on Tuesday morning to allow for the decay of short-lived natural activity. Following are the processing procedures.

1.1 Fill out an Environmental Data Card (see Appendix) for each gummed paper.

1.2 Cover the gummed side of the paper with a thin layer of commercial plastic wrap. Several steps are involved.

1.2.1 Lay the paper, gummed side down, on the plastic wrap so that the gummed surface is completely covered (Fig. 1.9-2). If the gummed paper is wet, allow to air dry before covering with plastic wrap. HANDLE ONLY THE EDGES OF THE GUMMED PAPER. In adverse weather conditions, the gummed paper tends to become brittle and may break. If this occurs, the paper should be treated with special care and placed on top of the wrap as under normal conditions.

1.2.2 Press gummed paper firmly against the plastic wrap.

1.2.3 Cut gummed paper from its aluminum frame and label the nongummed side with the LAM station number, which can be found on each sample's aluminum frame.

1.2.4 Cut all excessive wrap from gummed paper (i.e., no double layers of wrap) and place on top of a 0.38- by 0.43-m cardboard backing with the gummed side up. Tape the wrapped paper to the cardboard and label for identification purposes.

1.3 The gummed fallout paper should be autoradiographed to locate radioactive tracks.

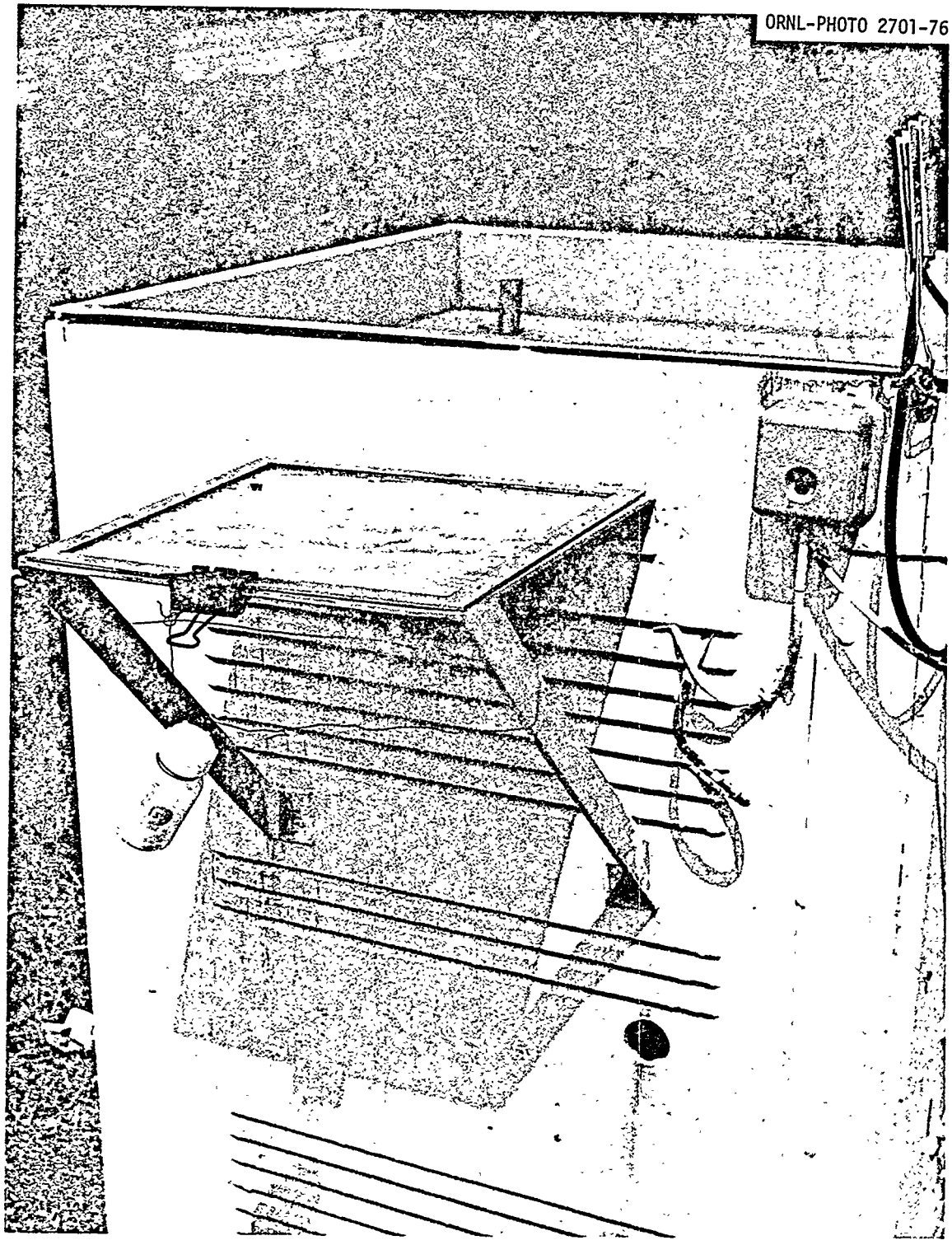

Fig. 1.9-1. LAM gummed fallout papers.

Fig. 1.9-2. Gummed paper samples being processed.

1.3.1 Autoradiographic techniques

1.3.1.1 In the dark room, use a graphite pencil to label the film with the date and LAM station number. Label the cardboard and film so that the gummed paper can be identified as to the exact position of the radioactive tracks on the film. THIS IS EXTREMELY IMPORTANT WHEN TRYING TO DETERMINE THE SPECIFIC LOCATION OF RADIOACTIVE TRACKS. Place each gummed paper (on cardboard) on a 0.45- x 0.45- x 0.01-m wooden board and cover with a sheet of 0.35- by 0.43-m Kodak Blue Brand X-Ray film (type BB-5). Place film on the sample such that the gummed side is in direct contact with it. Cover the film with a sheet of film packing paper to prevent scratching.

1.3.1.2 Stack the gummed fallout paper one on top of the other as described in step 1.3.1.1. Place a wooden board on the top of the last sheet of film packing paper and expose the film to gummed paper for a period of 24 h. DO NOT TURN ON LIGHTS.

1.3.1.3 After 24 h, place each film in an individual film rack. Keep all film baths at a constant temperature of 20°C (68°F) and wear gloves while developing.

1.3.2 Procedures for developing films

1.3.2.1 Place each film in the developer* bath for exactly 3 min. Space films so that the developer will coat both sides of the film.

*Coronex X-Ray Developer and Replenisher by Du Pont. The commercial package mixture is used.

1.3.2.2 Place immediately in a stop-bath solution of 1N CH_3COOH for 1 min.

1.3.2.3 Remove, drain, and immerse immediately in the fixer* for 10 min.

1.3.2.4 Remove from fixer, drain, and place immediately in the wash bath for 45 min.

1.3.2.5 Remove, drain, and allow to dry in the oven for 1 h; separate the films while in the the furnace to ensure complete drying.

1.4 After the films have been processed, check films individually on a light box for tracks caused by ionizing emissions. In cases where tracking occurred, record the number of spots according to their sizes for permanent record. Compare each sample film strip with a calibrated film strip that has the characteristic spot sizes of the activities. This comparison aids in the determination of the magnitude of each radioactive particle detected. The calibrated film strip is exposed to standard reference sources of known activities in the ranges of 10^5 to 10^6, 10^6 to 10^7, and greater than 10^7 dis/min for 24 h (dis min^{-1} $24h^{-1}$). Each spot created by these activities has a characteristic size and can, therefore, be used to qualitatively categorize each particle activity detected on the sample. The contaminated gummed filter paper(s) can then be assayed for quantitative identification of radioactivity detected. This is done by the Analytical Chemistry Division using either solid state detection systems (for gamma and/or alpha spectrometry) and/or radiochemical techniques.

1.5 For those gummed papers on which little or no tracking occurs, coat papers (with wrap) completely with a layer of scintillate mix on the gummed sides for gross-beta counting.

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*Coronex X-Ray Fixer by Du Pont. The commercial mixture is used.

1.6 Procedures for the preparation of gummed fallout paper samples for liquid scintillation counting.

1.6.1 Reagents

1.6.1.1 Toluene base

1.6.1.2 PPO (2, 5-diphenyloxazole)

1.6.1.3 POPOP (1, 4-bis-2-5-phenyloyazoyl)

1.6.1.4 Cellulose acetate

1.6.2 To obtain a high counting efficiency for tritium, a nonpolar solvent, toluene, is used as the base in the liquid scintillation mixture. PPO and POPOP are used as the primary and secondary scintillators, respectively, so that the photon spectrum will match the spectral sensitivity of the photomultiplier tube. The addition of cellulose acetate ensures adhesion to the sample without increased quenching. The liquid scintillation mixture provides a maximum sensitivity for counting.

1.6.3 Procedure

1.6.3.1 Pour 1000 ml of toluene base into a 1500-ml beaker.

1.6.3.2 Add 50 g of crushed polyethylene vials and stir until completely dissolved.

1.6.3.3 Add 5 g of PPO and 100 mg of POPOP.

1.6.3.4 Transfer the mixture into a 4000-ml, light-insensitive, storage bottle for future use.

1.6.3.5 Store in a dark area. Brush the mix on and allow to air dry for 5 min. After the scintillate has dried, cut each gummed fallout paper in half. Fold each half and place into a separate 24-ml cellulose acetate

counting vial labeled to identify the sample pairs.

1.6.3.6 Count each vial for 10 min in a Packard Tri-Carb liquid scintillation spectrometer unit. A background counting rate in the order of 15 to 20 counts/min is obtained using the system when counting for gross-beta activity (integrate mode). Use a reference sample to determine the efficiency of the detector before the samples are counted. Spread the reference source uniformly over a 0.30- by 0.30-m gummed fallout paper (on the gummed side) and wrapped with a thin layer of plastic wrap. Coat with a layer of the scintillation mix used for the field samples. Cut the reference sample in half, place in two separate cellulose acetate vials, and count to duplicate the geometry between reference source and field samples. The efficiency for this method is from 15 to 20%.

1.6.3.7 After a permanent record has been filed for each gummed fallout paper (both halves summed), the papers are discarded.

2. PAM

The PAM gummed fallout papers follow the same analysis procedure as the LAM papers except they are not autoradiographed. They are covered with plastic wrap and coated with scintillate for gross-beta counting. The PAM gummed fallout papers are exchanged on Monday; the processing of this paper begins on Wednesday morning.

3. RAM

The RAM gummed fallout papers are processed exactly as the PAM gummed fallout papers. Processing begins when they are received through the mail.

1.10 Specific Radionuclide Analyses Applied to Air Monitoring Samples

1. Sample Preparation

Air monitoring filters from the local (LAM), perimeter (PAM), and remote (RAM) air monitoring networks are changed at weekly intervals and gross-alpha and -beta determinations are made on individual filters (Sect. 1.9). Quarterly (13-week) composites are then made of the individual filters from each of the LAM, PAM, and RAM collections. The LAM quarterly composites consist of 23 stations yielding 299 filters for the quarter. Filters from 5 weeks of the quarter (115 papers) are placed in a 6.5 x 6.5 x 3.0 cm polystyrene box. The remaining filters are evenly divided into two 4-week packages (92 papers each) in polystyrene boxes identical to that used for the 5-week collection. The resultant LAM quarterly composite has three components: a 5-week box with 115 papers and two identical 4-week boxes with 92 papers each.

Similar considerations are used in preparing composites from the PAM and RAM networks. Quarterly composites from both these latter networks are divided into two segments: a 7-week portion and a 6-week portion. These filters are fitted into two of the 6.5 x 6.5 x 3.0 cm boxes for later counting in the high-resolution gamma-ray spectrometer.

2. High-Resolution Gamma-ray Spectrometer

The gamma-ray spectrometer system currently used to analyse radionuclides in air monitoring samples consists of a 23% efficient [relative to a 7.6 x 7.6 cm NaI(Tl) detector at 25 cm for 1.33 MeV gamma rays] germanium-lithium detector with a resolution of 2.2 keV full width at half maximum for 1.33 MeV gamma rays. The detector is housed in a lead shield with graded liner and wall thickness of 7.6 cm. The entire spectrometer system is contained within a counting facility with high-density, 61-cm thick concrete walls and ceiling.

The detector is operated with suitable low-noise electronic assemblies and is connected to a Nuclear Data, Inc. Model 4420

computer-based pulse-height analyzer. The operating software for the system is ND 1076-02 (1976). Operating parameters are chosen so that 0.5 to 0.7 keV per channel gain calibration is selected and a total channel capacity of 2048 to 4096 region is used. With such a choice of conditions, the spectrometer may detect gamma rays within the energy range of 60 to 2700 keV.

Energy calibration is performed with the on-line procedure selected by the operating monitor. Mixed radionuclide standards such as U.S. National Bureau of Standards' SRM 4216 are convenient for this purpose.

3. Efficiency Calibration

Three permanent calibration standards for air monitoring samples were prepared by tagging a cation exchange resin (Dowex 50) with suitable radionuclide standards by batch equilibrations. Portions of the air-dried resins (previously assayed by direct comparison with U.S. National Bureau of Standards materials) are placed in 6.5 x 6.5 x 3.0 cm boxes identical to those of the quarterly composites. Standardization aliquots are adjusted so that a quantity of ion exchange resin will fill one of the calibration boxes to the same height as the 5-week box of the LAM composites. The other two boxes are filled with a quantity of calibrated resin equivalent to the 4-week boxes of the LAM collection.

Before analysis of any of the quarterly composite air samples, calibrations are performed by placing the 5-week calibration box on the top of the end cap of the germanium-lithium detector and putting the two 4-week boxes in a close-packed array against the side of the end cap. Data are collected for a suitable time interval depending on the strength of the calibration sources (1000 to 2000 records). An efficiency versus energy curve is constructed for the three-box calibration and used in later analysis of the LAM network composites. A second calibration curve is made by placing the 5-week calibration box on the top of the end cap of the germanium-lithium detector and putting one of the 4-week boxes against the side of the germanium-lithium end cap. This latter efficiency curve is used for both the PAM and RAM network composites.

4. Data Collection

The prepared samples of quarterly composite air filters are placed in the detector shield in an array exactly like that used for the calibration sources (LAM composite with three boxes in close-packed array and PAM and RAM composites in identical two-box arrays). Counting intervals for each of the three composites are at least overnight (55,000 s).

At the conclusion of the preset counting interval, data for the given composite is entered onto industry-compatible nine-track magnetic tape for subsequent processing by an off-line computer program. In addition, a PEAK SEARCH routine from the ND 1076-02 monitor is performed on the spectral data while it resides in the ND 4420 memory. The on-line PEAK SEARCH determines the area, background, centroid, full width at half maximum, and the energy of each peak in the spectrum. The on-line program provides an immediate readout and the data is useful for quality control or other purposes. To produce quantitative results, the area determined for each peak must be corrected for efficiency, branching ratio, and sample weight.

The IBM 360 program used for data reduction is called MONSTR. It is operated in a batch mode and utilizes spectral data and experiment parameters submitted on compatible magnetic tape. The initial stage of MONSTR performs a peak extraction in a fashion similar to the on-line program. However, MONSTR contains routines for efficiency correction and nuclide identification, so the final output lists the identity of each major nuclide along with a quantitative determination of its concentration. Detailed comparisons have shown that the basic functions of both programs yield similar results. Hence, both programs are used in a complementary fashion in the overall data reduction schemes for air filter analyses.

In a typical air filter sample from any one of the three networks, beryllium with a 477.6 keV gamma ray is usually present at a total activity of [(5.55 to 9.25) x 10^2 Bq] [(1.5 to 2.5) x 10^{-2} μCi]. Other nuclides usually detected are: cerium-144 with a 133.5 keV gamma-ray, cesium-137 (661.6 keV), and antimony-125 (428, 464 and

600.8 keV). At times of atmospheric nuclear testing, other short-lived fission products may be measured with variable sensitivity.

Quantitative results calculated for each radionuclide are corrected for decay from the time of counting back to the midpoint of the respective quarter: February 15, May 15, August 15, and November 15, for the first, second, third, and fourth quarters respectively.

Final calculations for the air monitoring data involve determination of the total volume of air passing through each of the composites in the 13-week interval. Such determinations yield approximately 1.2 x 10 cm^3 for a typical LAM sample, approximately 1.9 x 10 cm^3 for a typical PAM, etc. Thus, specific radionuclide concentrations are calculated by dividing the total activity for that specific nuclide by the total air flow through the composite. Results may be expressed as Bq/cm^3, Bq/liter, Bq/m^3, etc.

1.11 Gross-Alpha and Gross-Beta Counting of the Hollingsworth and Vose-70 Filter Paper

Filter papers from the LAM, PAM, and RAM stations are counted for both gross-alpha and gross-beta activities. The filter papers are usually counted the day following collection, after the short-lived natural activities have essentially decayed. The following procedure is used for determining both gross-alpha and gross-beta activity.

1. Each filter paper is dried, if wet, and sent to the counting room with its respective computerized environmental data card in an envelope.
2. In the counting room, the papers are cut (in half) parallel to the particle grids to prevent contamination of the scissors.
3. Each 6.25 x 12.5 cm filter paper is placed in a ZnS(Ag) scintillation detector and counted for 1 min. The detector drawer has been modified so that each half of the filter paper sample fits snugly. The detector has an efficiency of approximately 50% and a background counting rate of 0.5 counts/min.
4. The net count rate of both halves of each filter paper is summed. The total activity of the filter paper in Bq (μCi) gross-alpha is recorded on the computerized environmental data card.
5. After the gross-alpha activity has been determined, each half of the filter paper sample is trimmed to 5 x 10 cm (by removing the borders) and placed in a separate 25-ml cellulose acetate vial for gross-beta counting. These scintillation vials are coated internally with a plastic scintillation phosphor mixture. The procedure for the preparation of this mixture is presented in Sect. 1.9.
6. Each vial is counted for 10 min in a Packard Tri-Carb liquid scintillation spectrometer unit that has a background counting rate of 15 to 20 counts/min. To confirm the efficiency of the system, a reference sample is counted before counting the filter samples. The efficiency will vary according to the energies of the polyenergetic beta particles.

7. The total net count rate for both halves of each filter paper sample is converted to Bq (μCi) units of gross-beta and recorded on its respective environmental data card.

8. Each filter paper sample (both halves) is placed in its respective envelope and kept on file until the end of the quarter, when a quarterly composite assay of long-lived activity present on the filter papers for each of the LAM, PAM, and RAM networks is performed. This composite assay includes gamma spectrometric analyses and radiochemical analyses for strontium, plutonium, uranium, and thorium radionuclides.

1.12 Procedure for Preparing and Reading Thermoluminescent Dosimeters

Various methods can be used to anneal, temper, and read thermoluminescent dosimeters (TLDs), and it is important that the same procedure be followed each time for accurate results. Because there are various types of TLDs available, different procedures frequently are needed to prepare them for their specific uses. A general procedure for preparing and reading TLDs for environmental on-site monitoring of radiation at ORNL follows. This procedure is followed for all three types of TLDs used in the field: TLD-100s, -200s, and -700s.

1. Preparation of TLDs to Be Put Into Service

1.1 Handling. Proper care is needed to prepare the TLDs for dosimetry readings.

1.1.1 Clean the metal plate heating discs with isopropyl alcohol and dry them using an air hose before placing the TLDs on them.

1.1.2 Handle the TLDs with a pair of tweezers or a vacuum hose rather than by hand.

1.2 Annealing. Two ovens are used to anneal the TLDs. One is heated to 400°C; the other is heated to 100°F. It is important that the timing be accurate. TLDs are to be treated essentially the same way.

1.2.1 Place all the TLDs needed (including background and calibrated TLDs) on the metal heating plate.

1.2.2 At 400°C, anneal the TLDs for 30 min ± 15 s.

1.2.3 Remove from the oven and allow to cool for 3 min on a brass plate. TLDs are sensitive to light and should be covered when outside the oven.

1.2.4 After cooling, place the TLDs in the second oven at 100°F for 2 h ± 5 min.

1.2.5 Allow the TLDs to cool before placing into the 135-ml plastic bottles for the field.

2. Loading the TLDs for Field Dosimetry

Each type of air monitor requires a specific set of TLDs; therefore, the procedure for loading the TLDs for field dosimetry purposes will be presented for each type of air monitor.

3. Local Air Monitors (LAMs)

Place three annealed TLD-100 chips in a plastic TLD ring and cover with a round foam pad before sealing the ring (Fig. 1.12-1). Place the ring carefully into a 135-ml plastic bottle and add tissue paper to hold the ring in place. Desiccant is also placed in the bottle. Seal the bottle and label it with a red or yellow dot (which indicates a yearly or quarterly exposure period respectively) and with the number of the LAM station.

In addition to the TLD field samples, three background and three calibrated TLD-100 samples are prepared to accurately measure the integrated dose from the field samples. The background and calibrated TLD samples are prepared the same way as the field samples. The three calibrated TLD samples are exposed to a radium-226 reference source at a known distance and period of time. Therefore, the readout can be calibrated to the theoretical integrated dose (millirems). Other factors such as backscattering must also be taken into account. This calibrated exposure is performed during the middle of the long-term exposure period for the field samples. They are stored in a lead pig until all the LAM field samples are ready to be analyzed.

The three background TLD samples are not exposed to any radiation other than background levels. They are placed in the lead pig (along with the calibrated TLD samples) at the midpoint of the long-term exposure period of the field samples. Therefore the net dose can be determined by subtracting the background integration from the counts of the calibrated TLD samples.

4. Perimeter Air Monitors (PAMs)

Place two annealed TLD-200 chips between 2-cm layers of cadmium filter in a plastic TLD ring; no foam padding is necessary. Handle

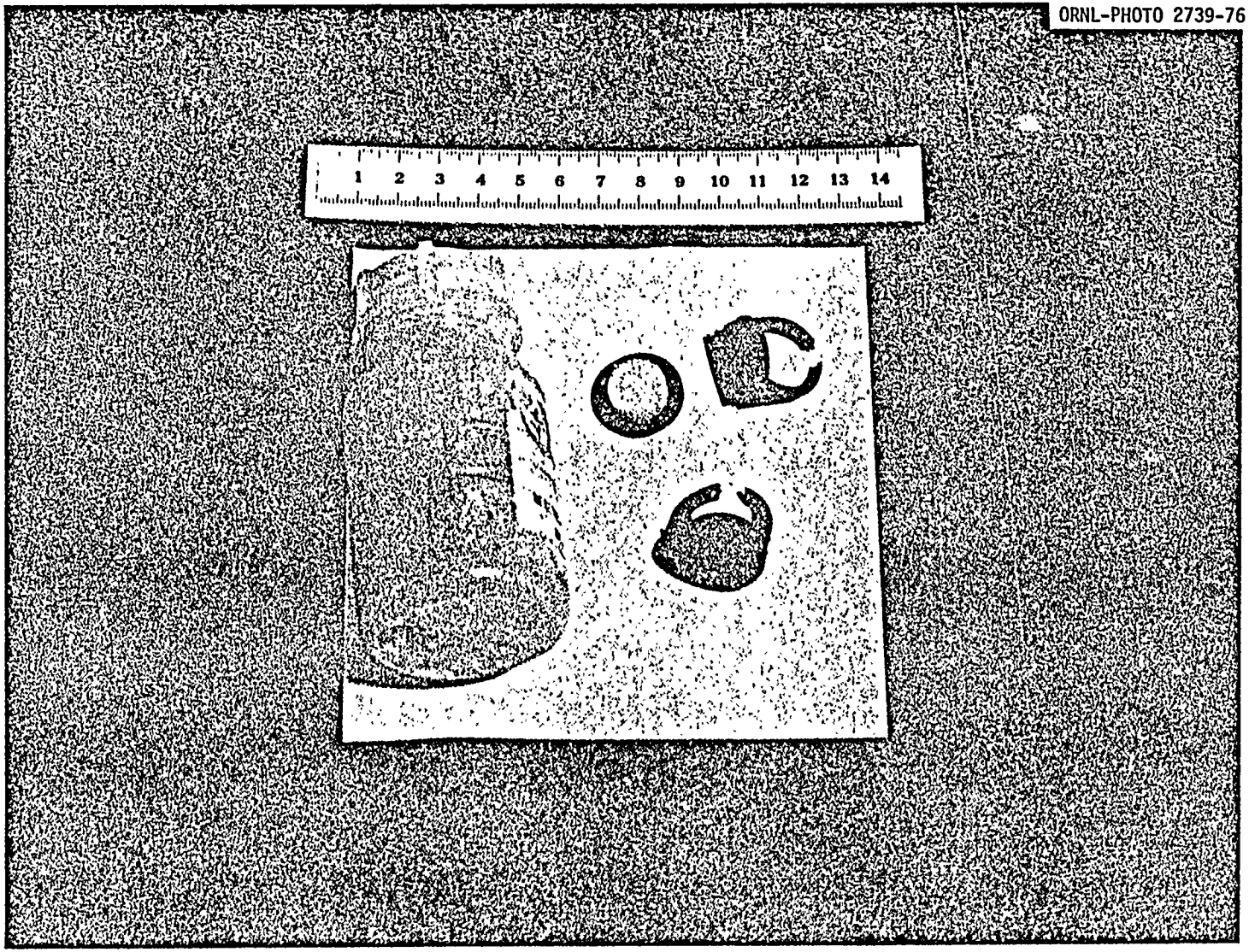

Fig. 1.12-1. Plastic TLD rings.

the chips with a vacuum rather than by hand and place the ring and tissue paper into a plastic bottle. Seal the bottle and label with the PAM station number.

Three background and three calibrated TLD-200 field samples are also prepared in addition to the field samples. Each sample consists of a single TLD-200 chip between two cadmium filters. The samples are prepared the same as the field samples. From this point on, the procedures for preparing the background and calibrated samples are the same as those presented for the stations.

5. Remote Air Monitors (RAMs)

Place three annealed TLD-700 chips in a plastic TLD ring and cover with a round foam pad prior to sealing the ring. These chips are used for the annual long-term exposure samples. The ring is then packaged as presented earlier.

In addition to the annual long-term exposure, a field sample is replaced every 6 months. Two annealed TLD-200 chips are sandwiched between two layers of cadmium filter and placed in a plastic ring. The ring is packaged in the same manner as presented earlier.

Three background and three calibrated samples are prepared identical to both the TLD-200 and -700 chips. The calibrated samples are exposed during the middle of the long-term exposure period of the field samples. They are stored in a lead pig, along with the background samples, until all the RAM field samples (semiannual and/or annual term exposure samples) have been collected for analysis.

6. Reading the TLD Field Samples

When the TLD field samples are returned to ORNL, the TLDs are removed from the plastic bottle and placed into separate envelopes. Each envelope is labeled with the initial and final date that the sample was exposed and the location of exposure. The envelopes are placed in the lead pig along with their respective background and calibration samples. The LAM field samples and their calibrated and background samples are read together. The following procedure is used when reading the three types of TLDs.

6.1 Temper all TLDs at 80°F for 20 min.

6.2 Cover the TLDs and allow to cool for 3 min.

6.3 Preheat the TLD reader (Eberline Model TLR-5) from 130 to 135° for 13 to 15 s. The integration temperature ranges from 280 to 285°C for 12 to 15 s.

6.4 Place the TLDs in the TLD reader and determine the total integrated dose (Fig. 1.12-2).

Because the three background samples and three calibrated samples are also read, an accurate integrated dose for the exposed field samples can be determined.

The procedure outlined above is also used for both the PAM and RAM field samples. In the case of the PAMs, the field samples can be collected in a day. Therefore, the integrated dose for each sample can be evaluated using the same background and calibrated doses for each sample. This is not the case with the RAM field samples. Only two field samples are collected each week; therefore, a total of 5 weeks is required to collect all the RAM field samples. Those samples which have been collected prior to the last week of collection are stored in the lead pig along with their background and calibrated samples. When evaluating the actual net integrated dose for each field sample, a correction factor for the time that each field sample was exposed to background radiation (i.e., stored in the lead pig) must be used. This correction factor is the ratio of the number of weeks the RAM TLDs were stored in the lead pig to the number of weeks the background TLDs were taken. The counts obtained from this ratio are subtracted from the counts of the RAM TLDs. This value is the actual net integrated dose of the field TLDs.

7. Records

Accurate records must be kept of the TLD samples. These include the length of time the field samples have been exposed and the location of exposure. The dates and exposure doses must be recorded on calibrated samples. The dates that the background samples were stored in the lead pig must be recorded on samples so that the proper

Fig. 1.12-2. The dosage of low level radiation at which TLDs are exposed can be determined by a TLD reader.

correction factors can be applied and the accurate field sample dose can be determined. A permanent record for each field sample (in millirems) must be logged in the laboratory notebook.

1.13 Procedure for the Preparation and Analysis by Gamma Spectrometry of Activated Charcoal for Iodine-131 and other Fallout Radionuclides

The activated charcoal cartridges (Fig. 1.13-1) at the LAM and PAM stations are collected, replaced, and returned to the Environmental Surveillance Laboratory weekly. The activated coconut charcoal in each cartridge is poured into separate 70 x 15 mm plastic petri dishes and covered. The petri dishes are labeled with the date and number of the LAM or PAM on the charcoal cartridge and are sent to the Analytical Chemistry Laboratory (along with a request sheet UCN-1910) for analysis of iodine-131 and other fallout radionuclides. The charcoal samples should be processed as soon as possible because of the short half-life of iodine-131 (approximately 8.05 days).

After Analytical Chemistry receives the labeled samples, they are counted, separately, on 7.5 x 7.5 cm NaI(Tl) crystals. Three separate detection systems (crystal, pulse-height analyzer, etc.) are used so that three samples can be counted (one for each system) at any one time. The three photopeak spectra are fed into the Nuclear Data (ND) 6600 computer and resolved for the radionuclides identified on each sample.

The petri dish containing the sample is placed directly on top of the crystal and is counted from 40 to 90 min. Each crystal is housed in a lead pig constructed of an inner graded shield with layers of copper, cadmium, and 7.5 cm of lead. This design helps to reduce interaction between the crystal and low energy rays and/or gamma rays from cosmic and lead emissions. The counting room is constructed with 60-cm thick low-activity, high-density concrete.

A reference source of iodine-131 adsorbed on activated coconut charcoal (6-14 mesh) is placed in a petri dish (simulating a field sample) and counted on the crystal in the same manner as the field samples. The photopeak spectrum may be resolved by using reference sources from the library of standards. The photopeak may also be resolved by least-squares using the Alpha-M computer program presented in "A General Discussion of the MONSTR Program for Determining Radionuclides in Germanium-Lithium Gamma-Ray Spectra" (Sect. 2.4). The computer output lists those radionuclides identified in each sample.

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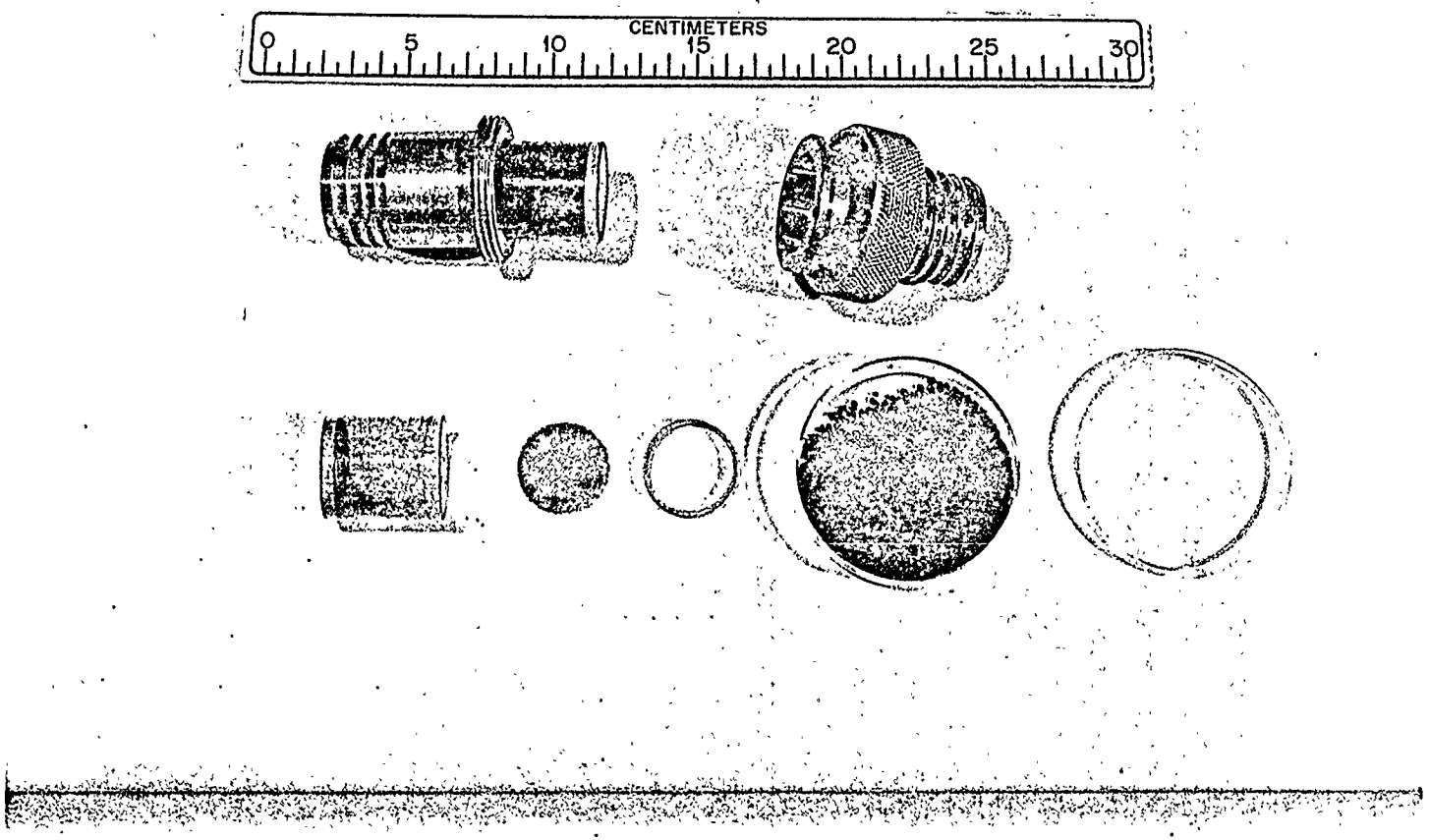

Fig. 1.13-1. Activated charcoal cartridges.

For improved sensitivity, three 0.15 x 0.15 m NaI(Tl) crystals with approximately 3.5 x 7.5 cm wells in the center of each crystal are available for counting the samples. Specially fitted plastic vials with the same dimensions as the well are used to contain each charcoal sample. Each sample is fitted snugly into the well enabling a high geometry factor to be obtained. The spectrum developed is then fed into the ND 6600 computer along with its appropriate library of standards (reference sources counted in the 0.15 x 0.15 m crystal) and resolved. The sensitivity of this system for iodine-131 is around 20 dis/min ± 30% (for a 90-min count). The percentage error increases rapidly below this activity.

In the case where gamma spectrometry analysis by scintillation technique is too complex (e.g., nuclear fallout), the sample may be analyzed by a germanium-lithium drifted semiconductor detector to enable better resolution of the photopeaks.

Once the radionuclides and their activities have been determined, the charcoal samples are filed for two months, after which they are discarded. The concentrations of the radionuclides in the atmosphere may be determined by calculating the total volume of air that passed through the cartridge during the sampling period. Corrections for decay must also be taken into account (e.g., iodine-131 and its relatively short half-life). The results are sent to the Department of Environmental Management.

1.14 Radiochemical Method for Determining Plutonium in Air Filters (performed by Analytical Chemistry Division Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1 Scope and Application

This method is applicable to the determination of the isotopes of plutonium in paper and Hollingsworth type air filters.

2. Summary of Method

2.1 Plutonium-242 tracer is added to the dissolved filter solution and valence-adjustment steps are taken to equilibrate the tracer with the sample plutonium. After being adjusted to Pu^{+4}, plutonium is adsorbed on ion exchange resin, reduced to Pu^{+3}, and selectively eluted from the resin. Subsequently, plutonium is carried on praseodymium hydroxide, dissolved, and oxidized to Pu^{+4}, which is then extracted with thenoyltrifluoroacetone-xylene. The organic extract is evaporated on a stainless steel disk, and the plutonium is determined by alpha spectrometry.

2.2 The lowest concentration reported is 1.48×10^{-3} Bq/total (0.04 pCi/total). Typically, for filters that have filtered 1×10^{3} m^3 of air, the lowest concentration reported then is 1.48×10^{-6} Bq/m^3 (4×10^{-5} pCi/m^3).

3. Sample Handling and Preparation

Filter should be handled as little as possible to avoid loss of particulates and should be stored in plastic containers such as polyethylene bags.

4. Interferences

4.1 Plutonium-240 cannot be distinguished from plutonium-239 by alpha pulse-height analysis; however, alpha pulse-height analysis eliminates most other alpha interferences.

5. Apparatus

5.1 Analytical balance

5.2 Muffle furnace

5.3 Hot plate

5.4 Centrifuge

5.5 Vortex mixer

5.6 Extraction vials, 50-ml with plastic-lined screw caps

5.7 Teflon beakers, 250-ml size

5.8 Transfer pipettes

5.9 Lab glassware

5.9.1 Beakers, 250-, 100-, and 500-ml

5.9.2 Centrifuge tubes, 50-ml glass

5.9.3 Glass ion exchange column, 8 mm ID by 25 cm long, fitted with a stopcock and reservoir

5.10 Stainless steel disks

5.11 Multichannel analyzer system with silicon surface-barrier detector(s)

6. Reagents

6.1 Nitric acid (HNO_3), concentrated

6.2 Nitric acid (HNO_3), 8M: Add 500 ml of concd HNO_3 to 500 ml of water.

6.3 Ammonium hydroxide (NH_4 OH), concentrated

6.4 Plutonium-242 tracer solution: Dilute an NBS-certified (or equivalent) solution of plutonium-242 to a concentration of 10 dis/min/ml with 2M HNO_3 and store in glass.

6.5 Nitric acid, 1M: Add 62.5 ml of concd HNO_3 to 500 ml of water and dilute to 1 liter with water.

6.6 Sodium nitrite ($NaNO_2$), crystals

6.7 Sodium nitrite solution, 3M: Dissolve 10.4 g of sodium nitrite ($NaNO_2$) in water and dilute to 50 ml with water. Make fresh daily.

6.8 Thenoyltrifluoroacetone (TTA)-xylene solution, 0.5M TTA: Dissolve 111 g of $SC_4H_3COCH_2COCF_3$ (TTA) in xylene and dilute to 1 liter with xylene.

6.9 Ferric nitrate solution, 0.1M: Dissolve 40.4 g of ferric nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$] in water and dilute to 1 liter with water.

6.10 Hydroxylamine-hydrochloride solution, 5M: Dissolve 347.5 g hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in water and dilute to 1 liter with water.

6.11 Hydrochloric acid-hydroxylamine hydrochloride solution, 0.5M HCl-0.05M $NH_2OH \cdot HCl$: Add 42 ml of concd HCl and 10 ml of 5M $NH_2OH \cdot HCl$ to 500 ml of water and dilute to 1 liter with water.

6.12 Hydrochloric acid (HCl), concentrated

6.13 Praseodymium carrier solution: Dissolve 12.82 g of praseodymium nitrate dihydrate [$Pr(NO_3)_3 \cdot 2H_2O$] in 500 ml of water and dilute to 1 liter with water.

6.14 Anion exchange resin: Dowex 1 x 4 (50-100 mesh, chloride form) or equivalent

6.15 Hydrochloric acid (HCl), 8M: Add 666 ml of concd HCl to 334 ml of water.

6.16 Hydrogen peroxide (H_2O_2), 30% solution

6.17 Hydrofluoric acid (HF), concentrated

7. Procedure

7.1 Weigh an aliquot of the filter(s) and place in an adequately sized beaker. Relate weight to total sample to determine air-flow volume.

7.2 Place the beaker and sample in a muffle furnace and set the temperature to 210°C.

7.3 Carbonize the sample by allowing it to remain at 210°C for 8 h.

7.4 Raise the temperature of the furnace to 375°C and allow the sample to ash at this temperature for 16 h and finally ash at 525°C for 24 h.

7.5 Transfer the ashed sample to a 250-ml Teflon beaker.

7.6 Add 25 ml of concd HNO_3 and 25 ml of concd HF. Note — Paper filters may be completely soluble in HNO_3; therefore, the addition of HF may be excluded, and the procedure can be continued at step 7.14.

7.7 Place the sample on a hot plate and take to dryness.

7.8 Repeat steps 7.6 and 7.7 twice.

7.9 Add 15 ml of concd HNO_3 and take to dryness.

7.10 Repeat step 7.9 twice.

7.11 Take up the residue in 25 ml of 8M HNO_3 and 3 to 5 ml of 30% H_2O_2.

7.12 Transfer the sample to the original ashing beaker.

7.13 Place the beaker on a hot plate and digest with the addition of 30% H_2O_2 in 1-ml portions until the solution is clear.

7.14 Add 1.00 ml of 10 dis min^{-1} ml^{-1} plutonium-242 tracer solution.

7.15 Adjust the volume to about 50 ml and the acidity to 8M HNO_3 by evaporation and/or the addition of concd HNO_3.

7.16 Add 250 mg of $NaNO_2$ crystals, place on hot plate, bring to a boil rapidly, immediately remove from heat, and allow the sample to digest for 20 min to adjust the valence of plutonium to Pu^{+4}.

7.17 While the sample is digesting, prepare a resin column as follows:

7.17.1 Place a glass-wool plug in the bottom of the column described in step 5.9.3.

7.17.2 Slurry the resin (see step 6.14) with water and immediately discard the fines by decanting. Repeat as necessary until fines are removed.

7.17.3 Transfer 4 ml of resin to the column with water. Prevent any channeling by maintaining the solution level above the resin by use of the stopcock.

7.17.4 Place a glass-wool plug on top of the resin.

7.17.5 Convert the resin to the nitrate form by passing several column volumes of 8M HNO_3 through the column until the resin is free of chloride ions.

7.18 Transfer the sample solution, which should be at room temperature, to the prepared resin column, and allow it to flow through the column at a rate of 2 ml/min. Discard the effluent solution.

7.19 Rinse the beaker with 25 ml of 8M HNO_3 and transfer the rinse to the column. Allow the 8M HNO_3 rinse to flow through the column at a rate of 2 ml/min. Discard the effluent solution.

7.20 Rinse the beaker with 25 ml of 8M HCl and transfer the rinse to the column. Allow the 8M HCl rinse to flow through the column at a rate of 2 ml/min. Discard.

7.21 Add one drop of 0.1M $Fe(NO_3)_3$ and 1 ml of 5M $NH_2OH \cdot HCl$ to the column. Open the stopcock, and allow the solution to drain to the top of the resin bed; then stop the flow. Discard the effluent solution.

7.22 Add 4 ml of 0.5M HCl-0.05M $NH_2OH \cdot HCl$ solution. Place a 50-ml glass centrifuge tube under the column. Allow 3 ml of solution to drain into the tube and close the stopcock.

7.23 Allow 20 min digestion time for reduction of the plutonium to Pu^{+3}.

7.24 Add 25 ml of 0.5M HCl-0.05M $NH_2OH \cdot HCl$ solution. Pass the solution through the column at a flow rate of 2 ml/min into the 50-ml tube.

7.25 Add 1 ml of praseodymium carrier to the sample solution in the 50-ml tube and mix thoroughly.

7.26 Add concd NH_4OH, with stirring, to a pH of 9. Allow 15 min digestion time.

7.27 Centrifuge for 10 min at 1500 rpm and discard the supernatant solution.

7.28 Wash the precipitate with water, centrifuge, and discard the water wash solution.

7.29 Dissolve the precipitate in 6 drops of concd HNO_3 and transfer the dissolved sample to a 50-ml extraction vial with 5 ml of 1M HNO_3. Add 10 drops of 3M $NaNO_2$, mix well, and allow 20 min digestion time for plutonium to oxidize to Pu^{+4}.

7.30 Add 1 ml of 0.5M TTA-xylene solution and extract on a Vortex mixer for 10 min.

7.31 Centrifuge for 2 min to separate the phases. Discard the aqueous solution.

7.32 Scrub the TTA extract with 5 ml of 1M HNO_3. Centrifuge and discard the aqueous phase.

7.33 Transfer the TTA to a stainless steel disk placed on a hot plate set at 150°C. Allow the TTA to dry thoroughly.

7.34 Flame the stainless steel disk to a red heat.

7.35 Measure the alpha activities by pulsing with a silicon surface-barrier coupled to a multichannel analyzer.

8. Calculations

$$^{238}Pu = ACM/DE \quad , \quad Bq/m^3 \ ,$$

$$^{239}Pu = BCM/DE \quad , \quad Bq/m^3 \ ,$$

where

A = net integrated counts of ^{238}Pu from pulse analysis,

B = net integrated counts of ^{239}Pu from pulse analysis,

C = dis/min of ^{242}Pu added,

D = net integrated counts of ^{242}Pu from pulse analysis,

E = volume of air, m^3,

M = conversion factor to Bq; 1 Bq = 60 dis/min.

9. Precision and Accuracy

The precision is estimated to be ±20%. The accuracy has not been established.

Working Bibliography for Sect. 1.14

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Frederic B. Johns (ed.), *Handbook of Radiochemical Analytical Methods*, EPA-680/4-75-001 (February 1975).

1.15 Radiochemical Method for Determining Uranium in Air Filters (performed by Analytical Chemistry Division Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

This method is applicable to the determination of the isotopes of uranium in paper and Hollingsworth types of air filters.

2. Summary of Method

2.1 Uranium-232 tracer is added to the dissolved filter solution and equilibrated with the uranium in the sample. Plutonium and thorium are separated by adsorption on anion exchange resin under conditions that allow uranium to remain in the effluent. Repeated liquid-liquid extractions with methyl isobutyl ketone (hexone) are used to purify the uranium. The final hexone extract is dried on a stainless steel plate, and the determination of the uranium isotopes is made by alpha spectrometric measurements using a silicon surface-barrier detector to count the plate.

2.2 The lowest concentration reported is 1.48×10^{-3} Bq/total (0.04 pCi/total). Typically for filters that have filtered 1×10^{3} m^3 of air, the lowest concentration reported then is 1.48×10^{-6} Bq/m^3 (4×10^{-5} pCi/m^3).

3. Sample Handling and Preservation

Filters should be handled as little as possible to avoid loss of particulates and should be stored in plastic containers such as polyethylene bags.

4. Interferences

4.1 Iron in concentrations of milligrams per gram of sample tends to follow uranium throughout the chemistry and causes serious degradation of alpha measurements.

4.2 Uranium-234 cannot be distinguished easily from uranium-233.

5. Apparatus

5.1 Analytical balance

5.2 Muffle furnace

5.3 Hot plate

5.4 Centrifuge

5.5 Vortex mixer

5.6 Extraction vials, 50-ml with plastic-lined screw caps

5.7 Teflon beakers, 250-ml size

5.8 Transfer pipettes

5.9 Lab glassware

5.9.1 Beakers, 100-, 250-, and 600-ml

5.9.2 Centrifuge tubes, 50-ml glass

5.9.3 Glass ion-exchange column, 0.8 cm ID by 25 cm long, fitted with a stopcock and reservoir

5.10 Stainless steel disks

5.11 Multichannel analyzer system with silicon surface-barrier detector(s)

6. Reagents

6.1 Nitric acid (HNO_3), concentrated

6.2 Nitric acid (HNO_3), 8M: Add 500 ml of concd HNO_3 to 500 ml of water.

6.3 Aluminum nitrate solution [$Al(NO_3)_3$], 2.8M: Dissolve 1050 grams of aluminum nitrate nonahydrate [$Al(NO_3)_3 \cdot 9H_2O$] in a minimum of water with heat. Cautiously add 100 ml of concd ammonium hydroxide (NH_4OH) with stirring. Continue heating and stirring until all of the precipitate dissolves; dilute to 1 liter with water.

6.4 Sodium nitrite ($NaNO_2$), crystals

6.5 Methyl isobutyl ketone (hexone)

6.6 Potassium bromate ($KBrO_3$), crystals

6.7 Uranium-232 tracer solution: Dilute a stock solution of uranium-232 to a concentration of 10 dis min^{-1} ml^{-1}.

6.8 Anion exchange resin: Dowex 1 x 4 (50-100 mesh, chloride form) or equivalent

6.9 Hydrogen peroxide (H_2O_2), 30% solution

6.10 Hydrofluoric acid (HF), concentrated

7. Procedure

7.1 Weigh an aliquot of the filter(s) and place in an adequately sized beaker. Relate weight to total sample to determine air-flow volume.

7.2 Place the beaker and sample in a muffle furnace and set the temperature to 210°C.

7.3 Carbonize the sample by allowing it to remain at 210°C for 8 h.

7.4 Raise the temperature of the furnace to 375°C and allow the sample to ash at this temperature for 16 h; finally ash at 525°C for 24 h.

7.5 Transfer the ashed sample to a 250-ml Teflon beaker.

7.6 Add 25 ml of concd HNO_3 and 25 ml of concd HF.
NOTE — Paper filters may be completely soluble in HNO_3; therefore, the addition of HF may be excluded, and the procedure can be continued at step 7.14.

7.7 Place the sample on a hot plate and take to dryness.

7.8 Repeat steps 7.6 and 7.7 twice.

7.9 Add 15 ml of concd HNO_3 and take to dryness.

7.10 Repeat step 7.9 twice.

7.11 Take up the residue in 25 ml of 8M HNO_3 and 3 to 5 ml of H_2O_2.

7.12 Transfer the sample to the original ashing beaker.

7.13 Place the beaker on a hot plate and digest with the addition of 30% H_2O_2 in 1-ml portions until the solution is clear.

7.14 Add 1.00 ml of 10 dis min^{-1} ml^{-1} uranium-232 tracer solution.

7.15 Adjust the acidity to 8M HNO_3 by volume reduction and/or the addition of concd HNO_3.

7.16 Add 250 mg of $NaNO_2$ crystals; place on hot plate; bring to a boil rapidly; immediately remove from heat and allow the sample to digest for 20 min.

7.17 While the sample is digesting, prepare a resin column as follows.

7.17.1 Place a glass-wool plug in the bottom of the column described in step 5.9.3.

7.17.2 Slurry the resin (see step 6.8) with water and immediately discard the fines by decanting. Repeat as necessary until fines are removed.

7.17.3 Transfer 4 ml of resin to the column with water. Prevent any channeling by maintaining the solution level above the resin by use of the stopcock.

7.17.4 Place a glass-wool plug on top of the resin.

7.17.5 Convert the resin to the nitrate form by passing several column volumes of 8M HNO_3 through the column until the resin is free of chloride ions.

7.18 Transfer the sample solution, which should be at room temperature, to the prepared resin column.

7.19 Place a 250-ml beaker beneath the column and allow the sample solution to drain into the beaker at a flow rate of 2 ml/min.

7.20 Rinse the beaker with 25 ml of 8M HNO_3 and transfer the rinse to the column.

7.21 Allow the rinse to drain into the beaker also.

7.22 Place the beaker containing the column effluent on a hot plate and take to dryness.

7.23 Dissolve the residue in 10 ml of $Al(NO_3)_3$ solution and transfer to an extraction vial using a minimum of $Al(NO_3)_3$ to rinse the beaker.

7.24 Add an equal volume of hexone and extract on a Vortex mixer for 10 min.

7.25 Centrifuge for 2 min to separate the phases and discard the aqueous phase.

7.26 Add an equal volume of water and back-extract into the water on a Vortex mixer for 10 min.

7.27 Centrifuge for 2 min to separate the phases.

7.28 Transfer the aqueous phase to a 100-ml beaker.

7.29 Repeat steps 7.26, 7.27, and 7.28.

7.30 Place the beaker containing the water strip solution on a hot plate and take to dryness.

7.31 Add enough 8M HNO_3 to moisten the residue.

7.32 Add 10 to 20 mg of $KBrO_3$ crystals and digest for 10 min.

7.33 Dissolve and transfer the residue to an extraction vial with 5 ml of $Al(NO_3)_3$ solution.

7.34 Repeat step 7.24 using 1 ml of hexone; repeat step 7.25.

7.35 Transfer the entire hexone extract by drops to a stainless steel disk placed on a hot plate set at 100°C.

7.36 Flame the disk to a red heat.

7.37 Measure the uranium alpha activities by pulsing with a silicon surface-barrier detector and multichannel analyzer.

8. Calculations

$$^{238}U = AEM/DV, \text{ Bq/m}^3 ,$$

$$^{235}U = BEM/DV, \text{ Bq/m}^3 ,$$

$$^{234}U = CEM/DV, \text{ Bq/m}^3 ,$$

where

A = net integrated counts of ^{238}U from pulse analysis,

B = net integrated counts of ^{235}U from pulse analysis,

C = net integrated counts of ^{234}U from pulse analysis,

D = net integrated counts of ^{232}U from pulse analysis,

E = dis/min of ^{232}U tracer added,

V = volume of air, m^3,

M = conversion factor to Bq; 1 Bq = 60 dis/min.

9. Precision and Accuracy

The precision is estimated to be ±15%.

Working Bibliography for Sect. 1.15

J. E. Grindler, *The Radiochemistry of Uranium*, NAS-NS 3050 (March 1962).

F. B. Johns (ed.), *Handbook of Radiochemical Methods*, EPA-680/4-75-001 (February 1975).

1.16 Radiochemical Method for Determining Strontium in Air Filters (performed by Analytical Chemistry Division Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

This method is applicable to the determination of strontium-90 in paper and Hollingsworth types of air filters.

2. Summary of Method

2.1 Strontium carrier is equilibrated with the dissolved filter solution; afterward, the strontium is separated from calcium and magnesium by repeated nitrate precipitations. Additional purification is made by removing rare earths and other radionuclides by hydroxide scavenging and by removing barium and radium as chromates. Strontium is finally precipitated as the oxalate which is mounted for beta counting and counted on a low-background beta counter.

2.2 The lowest concentration reported is 2 pCi/total. Typically, for filters that have filtered 1×10^3 m^3 of air, the lowest concentration reported then is 7.4×10^{-5} Bq/m^3 (0.002 pCi/m^3).

3. Sample Handling and Preservation

Filters should be handled as little as possible to avoid loss of particulates and should be stored in plastic containers such as polyethylene bags.

4. Interferences

4.1 Strontium-89, when present in the sample, interferes with the beta counting of strontium-90. The presence of strontium-89 can be ascertained by absorption studies; the interference of strontium-89 can be circumvented by indirect determination of strontium-90 via the yttrium-90 daughter after adequate ingrowth.

4.2 Due to self-absorption, the counting efficiency varies with the amounts of solids which are counted on the mounts.

5. Apparatus

5.1 Lab glassware

5.1.1 Beakers, size adequate for sample

5.1.2 Centrifuge tubes, 50-ml glass

5.2 Centrifuge

5.3 Hot plate

5.4 Ice bath

5.5 Filter paper, Whatman No. 541 (11-cm)

5.6 Filter paper, Whatman No. 1 (18-mm)

5.7 Analytical balance

5.8 Filter flask and funnel

5.9 Fritted-glass filter crucibles

5.10 Desiccator

5.11 Low-background beta counter

5.12 Muffle furnace

5.13 Teflon beakers, 250-ml

6. Reagents

6.1 Acetic acid, 6M: Add 340 ml of glacial acetic acid (CH_3COOH) to 500 ml of water and dilute to 1 liter with water.

6.2 Ammonium acetate solution, 6M: Dissolve 462 g of ammonium acetate ($NH_4C_2H_3O_2$) in 500 ml of water and dilute to 1 liter with water.

6.3 Sodium carbonate solution, 2M: Dissolve 248 g of sodium carbonate monohydrate ($Na_2CO_3 \cdot H_2O$) in 700 ml of water and dilute to 1 liter with water.

6.4 Ammonium oxalate solution, saturated: Add 200 g of ammonium oxalate monohydrate [$(NH_4)_2C_2O_4 \cdot H_2O$] to 500 ml of water in a 1-liter container; dilute to 1 liter with water; mix thoroughly, and let stand overnight before using.

6.5 Sodium chromate solution, 1.5M: Dissolve 176 g of sodium chromate quadrihydrate ($Na_2CrO_4 \cdot 4H_2O$) in water and dilute to 500 ml with water.

6.6 Barium carrier solution, 10 mg Ba/ml: Dissolve 19.0 g of barium nitrate [$Ba(NO_3)_2$] in water and dilute to 1 liter with water.

6.7 Nitric acid (HNO_3), fuming

6.8 Ferric nitrate solution, 0.1M: Dissolve 40.4 g of ferric nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$] in water and dilute to 1 liter with water.

6.9 Nitric acid, 6M: Add 375 ml of concd HNO_3 to 500 ml of water and dilute to 1 liter with water.

6.10 Acetone (C_3H_6O)

6.11 Hydrofluoric acid (HF), concentrated

6.12 Ethyl alcohol (C_2H_5OH), 95%

6.13 Diethyl ether ($C_2H_5OC_2H_5$), anhydrous

6.14 Ammonium hydroxide (NH_4OH), concentrated

6.15 Strontium carrier solution: Dissolve 27.3 g of strontium nitrate [$Sr(NO_3)_2$] in a minimum of HNO_3 and dilute to 1 liter with water.

6.15.1 Standardization of strontium carrier: Pipette 5.00 ml of strontium carrier solution into a 100 ml beaker and add 30 ml of water. Adjust the pH to 9 with concd NH_4OH, add 10 ml of saturated $(NH_4)_2C_2O_4$ solution, and heat to nearly boiling with stirring. Cool to room temperature and quantitatively transfer the precipitate to a previously tared filter crucible with hot water. Wash the precipitate several times with hot water, three times with 10-ml portions of ethyl alcohol, and two times with 10-ml portions of diethyl ether. Desiccate the crucible and precipitate under vacuum to a constant weight. The net weight of the precipitate is the weight of strontium oxalate monohydrate ($SrC_2O_4 \cdot H_4O$) in 5.00 ml of the strontium carrier solution.

6.16 Phenolphthalein indicator solution, 5%: Dissolve 5 g of phenolphthalein ($C_{20}H_{14}O_4$) in 50 ml of 95% ethyl alcohol and dilute to 100 ml with water.

7. Procedure

7.1 Weigh an aliquot of the filter(s) and place in an adequately sized beaker. Relate weight to total sample to determine air-flow volume.

7.2 Place the beaker and sample in a muffle furnace and set the temperature at 210°C.

7.3 Carbonize the sample by allowing it to remain at 210°C for 8 h.

7.4 Raise the temperature of the furnace to 375°C and allow the sample to ash at this temperature for 16 h; finally ash at 525°C for 24 h.

7.5 Transfer the ashed sample to a 250-ml Teflon beaker.

7.6 Add 25 ml of concd HNO_3 and 25 ml of concd HF.
NOTE — Paper filters may be completely soluble in HNO_3; therefore, the addition of HF may be excluded and the procedure can be continued at step 7.14.

7.7 Place the sample on a hot plate and take to dryness.

7.8 Repeat steps 7.6 and 7.7 twice.

7.9 Add 15 ml of concd HNO_3 and take to dryness.

7.10 Repeat step 7.9 twice.

7.11 Take up the residue in 25 ml of 8M HNO_3 and 3 to 5 ml of 30% H_2O_2.

7.12 Transfer the sample to the original ashing beaker.

7.13 Place the beaker on a hot plate and digest with the addition of 30% H_2O_2 in 1-ml portions until the solution is clear.

7.14 Add 1.00 ml of the standardized strontium carrier.

7.15 Reduce the volume to approximately 15 ml and transfer to a 50-ml centrifuge tube.

7.16 Add 25 to 30 ml of fuming HNO_3.

7.17 Place the tube in an ice bath and stir the solution until precipitation is complete.

7.18 Remove the tube from the ice bath and centrifuge at 1500 rpm for 5 min. Decant the supernatant solution into a large volume of water and discard. Drain the tube completely, leaving a

minimum of HNO_3, as a precaution against any adverse reaction with the acetone wash which follows.

7.19 Add 30 ml of acetone and wash the precipitate thoroughly with stirring.

7.20 Centrifuge for 5 min at 1500 rpm and decant the acetone wash solution into a clearly marked, organic-waste container.

7.21 Dissolve the precipitate in a minimum of water.

7.22 Repeat steps 7.16 through 7.20 starting with the addition of fuming HNO_3 in step 7.16.

7.23 Dissolve the precipitate in 10 ml of water.

7.24 Add two drops of phenolphthalein indicator solution and 0.5 ml of 0.1M $Fe(NO_3)_3$ solution.

7.25 Add concd NH_4OH by drops with stirring until the phenolphthalein end point is reached, then add five more drops.

7.26 Centrifuge for 5 min at 1500 rpm.

7.27 Filter the supernatant solution through No. 541 filter paper into another 50-ml glass centrifuge tube; discard the precipitate. Record the time at which the filtering is done as the separation time of strontium-90 from yttrium-90. Wash the filter with 3 ml of water.

7.28 Neutralize the solution with 6M HNO_3, then add 1 ml of 6M acetic acid, 2 ml of 6M ammonium acetate, and 1 ml of barium carrier.

7.29 Heat the solution to near boiling, then add 1.5M Na_2CrO_4 solution by drops with stirring to precipitate barium chromate ($BaCrO_4$). Chill in an ice bath and stir to complete the precipitation. Check for complete precipitation of barium by adding a few more drops of Na_2CrO_4.

7.30 Centrifuge for 5 min at 1500 rpm.

7.31 Filter the supernatant solution through No. 541 filter paper into another 50-ml glass centrifuge tube and wash the filter with 3 ml of water. Discard the precipitate.

7.32 Add 2 ml of concd NH_4OH to the solution and heat to boiling.

7.33 Add 5 ml of saturated $(NH_4)_2C_2O_4$ solution with stirring to precipitate the SrC_2O_4.

7.34 Chill in an ice bath and continue to stir to complete the precipitation.

7.35 Centrifuge for 5 min at 1500 rpm and discard the supernatant solution.

7.36 Place a tared, 18-mm filter paper in the filtering funnel and wet with water using vacuum on the filtering flask.

7.37 Transfer the precipitate onto the filter with hot water; wash with two 10-ml portions of hot water, three 5-ml portions of 95% ethyl alcohol, and two 5-ml portions of diethyl ether.

7.38 Weigh the filter paper and precipitate, determine the chemical recovery, and mount for beta counting.

7.39 Count the sample mount without delay on a low-background beta counter.

8. Calculations

$$^{90}Sr = ABM/DV, \text{ Bq/m}^3 ,$$

where

A = net counts/minute of purified ^{90}Sr,

B = efficiency factor for ^{90}Sr, including self-absorption correction,

D = fraction of strontium carrier recovered,

V = volume of air, m^3,

M = conversion factor to Bq; 1 Bq = 60 dis/min.

9. Precision and Accuracy

The precision at the 95% confidence level is ±12%. The method exhibits a negative bias of 5% when applied to controls of known strontium-90 concentrations.

Working Bibliography for Sect. 1.16

M. A. Franson (ed.), *Standard Methods for Examination of Water and Waste Water*, 14th ed. (1976).

R. B. Hahn and C. P. Straub, "Determination of Radioactive Strontium and Barium in Water," *J. Am. Water Works Assoc.* 47(4), p. 335 (1955).

J. Kooi, "Quantitative Determination of Strontium-89 and Strontium-90 in Water," *Anal. Chem.* 30, 352 (1958).

1.17 Procedure for Monitoring Atmospheric Tritium

1. Introduction

In the atmosphere, tritium occurs primarily as water vapor (HTO) and as hydrogen gas (HT). To measure tritium in air (HTO and HT), one can use an ionization chamber or a gas proportional counter with filtered air introduced for internal counting. (The tritium betas produce ionization within the sensitive chamber volume.) This method is sensitive to tritium in all of its gaseous chemical forms. In another approach, HTO vapor is removed from the air with a bubbler or with a dessicant such as silca gel. The resulting tritiated water can be counted using liquid scintillation techniques.

Because of its high sensitivity, the silica gel-liquid scintillation method for HTO has been proposed as a standard method for the analysis of tritium in the atmosphere. (A detection limit of 2×10^{-5} pCi/cm^3 is reported.) The local air monitors (LAMs) contain a large air pump with extra capacity to incorporate the tritium-silica gel sampling apparatus as part of the station (Fig. 1.17-1). Presently, tritium monitors have been installed at LAM stations 6, 7, and 8.

2. Principle of the Method

A 30.5-cm-long by 3.2-cm diam aluminum cylinder is filled with 180 g of silica gel, which absorbs moisture up to 40% of its own weight. Air is pumped at 125 cm^3/min through the silica gel column (which collects essentially all of the moisture). The air flow is regulated with a needle value, and the flow rate is monitored with a flowmeter. A continuous sample can be taken over a two-week period using the same silica gel.

Following the sample collection, the silica gel is heated in a distillation flask to remove the moisture (Fig. 1.17-2). The distillate is counted in a liquid scintillation counter, and the concentration of HTO in the air is calculated.

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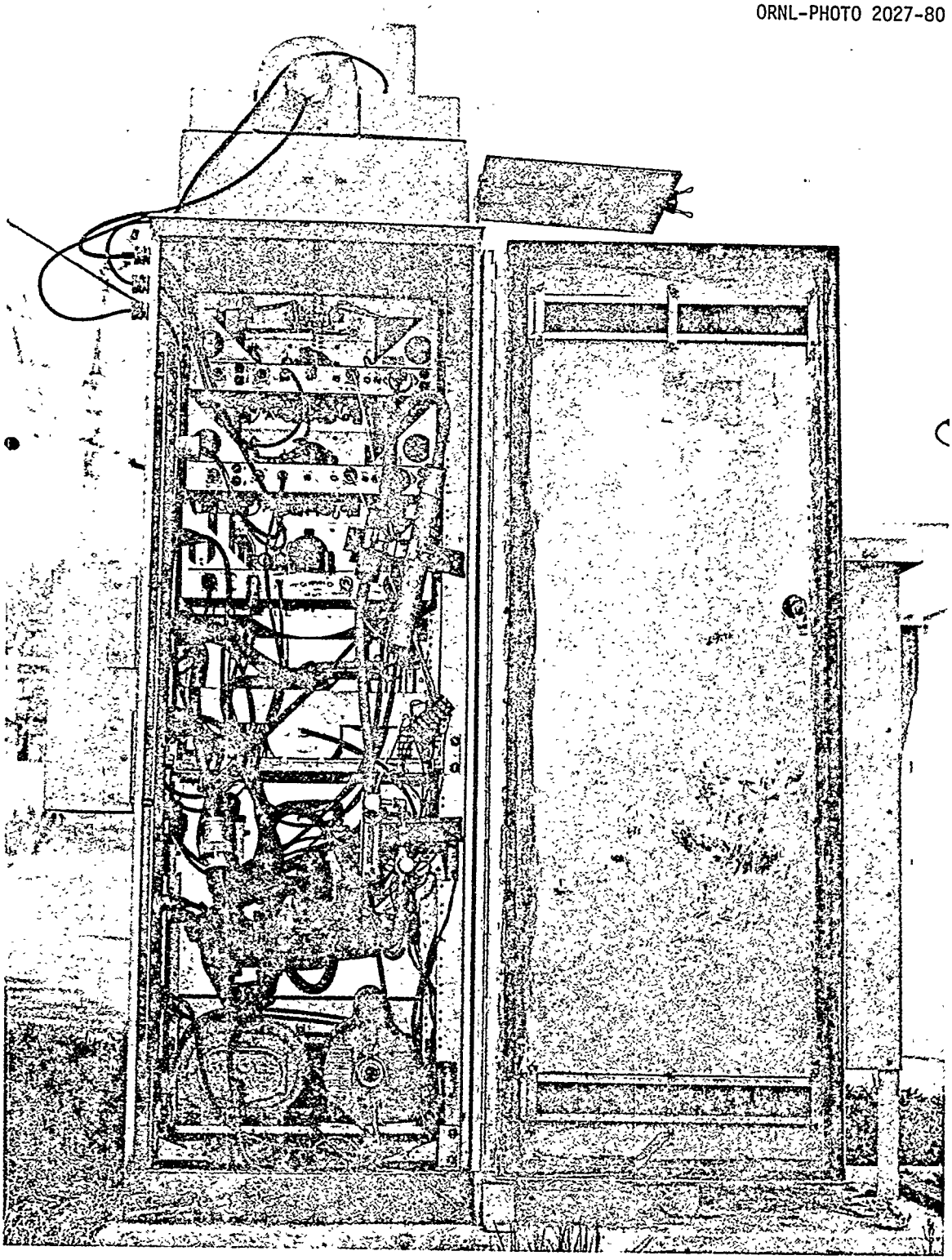


Fig. 1.17-1. Tritium sampling at LAM station.

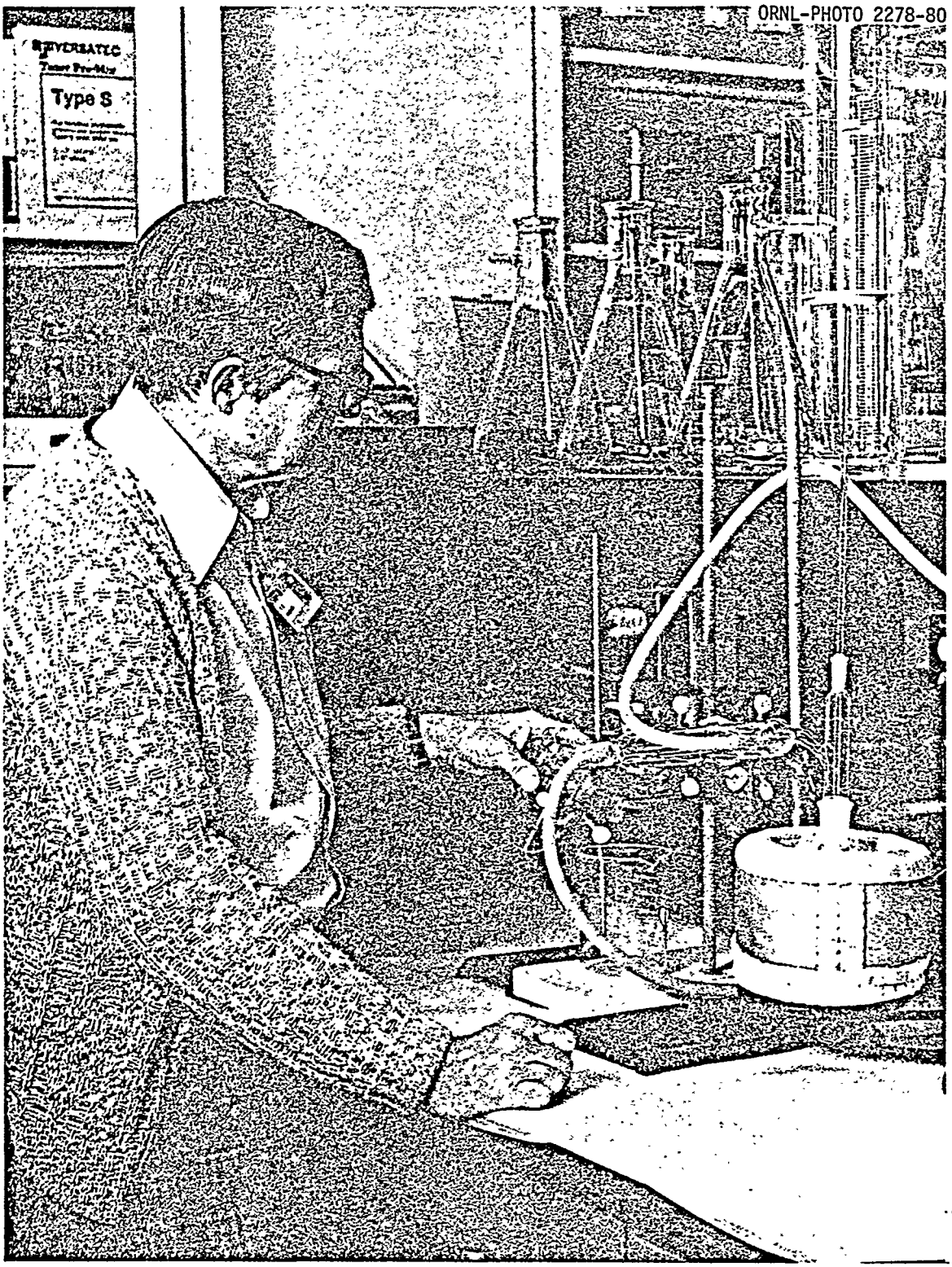


Fig. 1.17-2. Distillation of sample prior to tritium analysis.

3. Apparatus

3.1 Liquid scintillation beta counter

The Bioassay Group of IS&AHP counts the distillate using a Packard Tri-Carb liquid scintillation counting system.

3.2 Aluminum cylinders, 30.5-cm long by 3.2-cm diam; 6-16 mesh nonindicating silica gel

A 10-cm-long by 3.2-cm-diam clear plastic cylinder is filled with indicating silica gel (which indicates moisture by changing color) and installed downstream from the main cylinder. The indicating gel ensures that the sampling period was not long enough to saturate the silica gel.

3.3 Low-volume air pump, flow regulator, and flow rate indicator

3.4 Distillation flask and condenser

3.5 Miscellaneous apparatus such as counting vials, rubber stoppers, tubing, graduated cylinder, beakers, glass wool, heater for flask, and thermometer

3.6 Scintillation solution

4. Procedure

4.1 Fill the 30.5-cm aluminum cylinder with 180 g of nonindicating silica gel. Seal ends with wads of glass wood and No. 7 stoppers.

4.2 Remove stoppers at field sampling location. Insert one-hole stoppers in cylinder ends and connect tubing to air pump sampling system.

4.3 Insert indicating silica gel cylinder in-line between the collection cylinder and air pump.

4.4 Following sample collection, remove nonindicating silica gel cylinder and seal ends with No. 7 rubber stoppers for transport to the laboratory.

4.5 Pour silica gel into a 500-ml distillation flask.

4.6 Heat at 300°F until all moisture is removed (approximately three h).

4.7 Measure the total moisture collected and seal the sample in a bottle labeled with the sample identification and quantity (ml) of moisture collected. Complete a Request for Control Analysis Card and submit sample to the Bioassay Group of the IS&AHP Division for analysis. The Bioassay Group will provide the data on the sample and the counting system parameters necessary for calculating the HTO.

5. Calculations

5.1 Efficiency

$$E = \frac{S - B}{D}$$

where

E = counting efficiency,
S = counts per min of standard (in scintillation solution),
B = background counts per min of distilled water (in scintillation solution),
D = dis/min of standard.

5.2 Tritium concentration of the moisture

$$CM(Bq/ml) = \frac{C_s - B}{EVK}$$

where

CM = concentration of tritium in collected moisture (Bq/ml)
C_s = gross sample counts per min (i.e., summation of sample counts and background)
V = volume (ml) of sample counted
K = 60 (to convert dis/min to Bq).

5.3 The concentration of tritium oxide in air is calculated as follows, if silica gel (having 100% collection efficiency) is used and the flow rate is known.

$$CA(Bq/cm^3) = \frac{(CM)(W)}{F \cdot t}$$

where

CA = concentration of tritium oxide in air (Bq/cm^3),

F = flow rate (cm^3/min),

t = sampling time (min),

W = total volume of water collected (ml).

Working Bibliography for Sect. 1.17

Methods of Air Sampling and Analysis, Intersociety Committee for *A Manual of Methods for Ambient Air Sampling and Analysis*, American Public Health Association, Washington, D.C. 20036 (1972).

Osloond, J. H., J. B. Echo, W. L. Polzer, and B. D. Johnson, "A Tritium Air Sampling Method for Environmental and Nuclear Plant Monitoring," Proceedings of the Tritium Symposium, Aug. 30 through Sept. 2, 1971, Las Vegas.

1.18 Air Quality Determinations Using High-Volume Air Samplers

1. Introduction

High volume air sampling is the reference method for measuring particulate matter in ambient air. The following procedure describes the methodology of high volume air sampling, including system calibration, sampling technique, sample analysis, and calculations.

2. Calibration

2.1 The high volume air sampling stations (Fig. 1.18-1) at ORNL were calibrated at the time they were put into service, but this calibration should be verified once every 6 months and after installation of new brushes in the sampler motor. This procedure will be performed by the Instrumentation and Controls Division as follows.

2.1.1 Check the variac output voltage with an appropriate instrument. If significant departure from 90 V is observed, reset the variac such that 90 V will be delivered to the sampler motor. This operating voltage will greatly extend both motor and brush life.

2.1.2 Remove the faceplate of the filter holder and replace it with the calibration adapter plate. Attach the calibration orifice to the calibration adapter plate.

2.1.3 Connect the pressure recorder to the pressure tap on the side of the motor/blower unit. Install a clean recorder chart.

2.1.4 Connect the water manometer to the pressure tap of the calibration orifice.

2.1.5 Turn the sampler on and allow to run for five min.

2.1.6 Read the differential pressure as indicated by the manometer and record it on the data sheet in the column labeled "True H_2O."

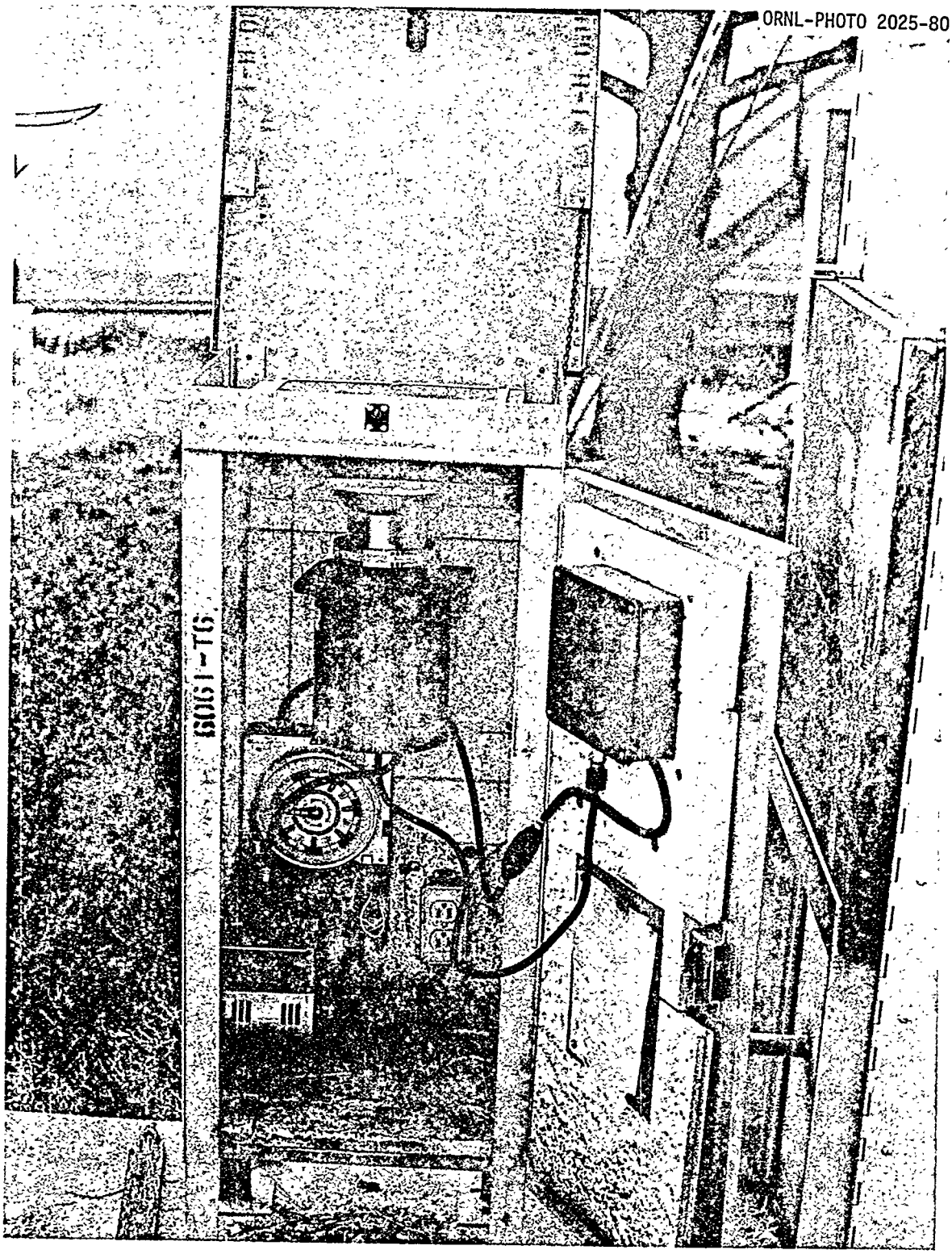


Fig. 1.18-1. High volume sampler.

2.1.7 Convert the differential pressure measurement to cubic feet per minute (cfm) using the calibration curve supplied with the calibration orifice.

2.1.8 Record cfm on the data sheet in the appropriate column.

2.1.9 Record the recorder chart deflection on the data sheet in the column labeled "Indicated."

2.1.10 Remove the calibration orifice from the adapter plate, insert the No. 18 resistance plate, then reattach the calibration orifice to the adapter plate.

2.1.11 Repeat steps 2.1.6 through 2.1.10 using the remaining four resistance plates.

2.1.12 Using the data obtained above, plot a calibration curve of cfm versus the recorder deflection (Fig. 1.18-2).

2.1.13 This new calibration curve may now be used as a direct reference for obtaining volumetric flow rates as a function of recorder deflection.

2.1.14 Repeat entire procedure for all sampling stations once every 6 months, directly after installation of new motor brushes, and at any time deemed necessary by extenuating circumstances.

3. Filter Preparation

3.1 Expose each filter to a light source (e.g., the type used to view x-ray films) and inspect for pinholes, particles, or other imperfections. Particles may be removed with a small brush. Filters with visible imperfections should not be used.

3.2 Place the inspected filter in a vacuum desiccator which contains a suitable amount of desiccant (e.g., Drierite or silica gel). Evacuate the desiccator (lab vacuum is sufficient) and allow the filter to equilibrate for 24 h.

3.3 Weigh the filter to the nearest tenth of a milligram (0.0001 g); record the tare weight and filter identification number in a suitable log book. Do not bend or fold the filter prior to sample collection.

ORNL-DWG 80-20363

CALIBRATION DATA SHEET

HIGH VOLUME AIR SAMPLER CALIBRATION

Unit No.:_____

Date:

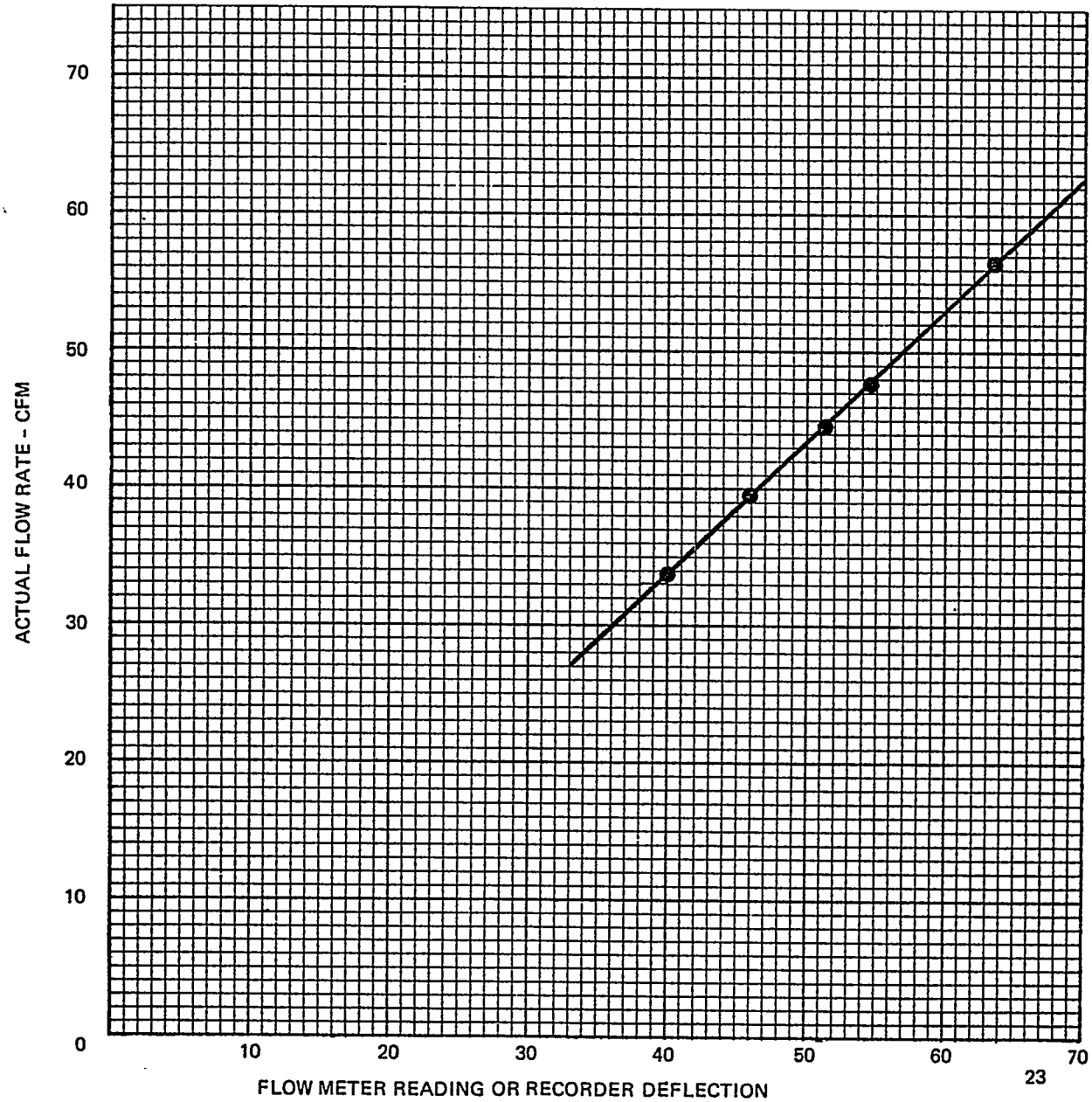
By:

Temp.: 60°F

At. Press: 28.55" H_2O

Remarks:

Plate	Indicated	True "H_2O	Actual cfm	
NONE	63.5	10.34	56.3	
18	54.7	7.66	47.6	
13	51.4	6.59	44.3	
10	47.1	5.12	39.8	
7	40.1	3.51	33.4	
5	33.2	2.22		



23

Fig. 1.18-2. Calibration data sheet for high volume samples.

3.4 The filter is now ready for sample collection. Exercise caution during transportation to sampling site to avoid damage to the filter.

4. Sample Collection

4.1 Open the shelter, loosen the wing nuts, and remove the faceplate from the filter holder. Wipe any dirt accumulation from around the filter holder with a clean cloth. Install a numbered, preweighed filter in position (rough side up), replace the faceplate without disturbing the filter, and fasten securely. Close the roof of the shelter.

4.2 Prepare the circular chart recorder as follows.

4.2.1 If a used chart is present, remove it carefully and transport it back to ORNL for later analysis.

4.2.2 Record the sampling date, start and stop set times, and the filter identification number on the back of the new chart prior to installation.

4.2.3 Clean any excess ink and moisture on the inside of recorder by wiping with a clean cloth.

4.2.4 Depress pen arm lifter to raise pen point and carefully insert a fresh chart in the recorder.

4.2.5 Carefully align the center tab of the chart to the drive hub of the recorder and press gently with thumb to lower chart center onto hub. Make sure chart is placed under the chart guide clip and the time index clip so it will rotate freely without binding.

4.2.6 With the pen arm lifter depressed, fill pen point reservoir with the ink provided. Place ink bottle nipple squarely against pen point reservoir and squeeze gently. Release pen arm lifter and let the pen point fall to the fresh chart. Move the pen arm laterally a few times to make sure the pen point will ink during the sampling period.

NOTE: On recorders supplied with a felt tip pen cartridge, make sure that the pen point rests on the chart with sufficient pressure to make a visible trace.

4.3 Set the timer in the shelter so the sampler will turn on and off at the predetermined times as follows:

4.3.1 To set the "on" time, place an "A" (bright) tripper on the dial face.

4.3.2 To set the "off" time, place a "B" (dark) tripper on the dial face.

4.3.3 Trippers must be tight against dial rim. Tighten tripper screws with fingers only.

4.3.4 To set time, grasp dial and rotate clockwise only until correct day and time of day appear at time pointer.

4.4 Manually trip time switch on to determine if sampler is operating properly and the recorder inking correctly.

4.5 When it has been determined that the unit is operating properly, turn unit off, reset timer, close timer door, close recorder door, and close shelter door being careful not to pinch the recorder tubing.

4.6 After the sample is complete, remove the faceplate as described above and carefully remove the filter from the holder, touching only the outer edges. Fold the filter lengthwise so that only surfaces with collected particulates are in contact and place in a suitable container for transport (such as a manila folder). If the sample is defective, void it at this time.

4.7 Record the average barometric pressure (mm Hg) and average temperature (°C) for the day of each sample in the log book. This information is available at the East Portal in the Shift Supervisors' Office.

5. Sample Analysis

5.1 Prepare the filter by equilibration in the vacuum desiccator (as described earlier) for 24 h.

5.2 After desiccation, weigh the filter to the nearest tenth of a milligram and record this value in the log book.

5.3 After weighing, the filter may be disposed of, stored as a permanent record, or submitted for further analysis (e.g., neutron activation).

5.4 Information in the log book, on the circular chart, and later in this procedure may now be used to calculate the mass concentration of suspended particulates (SP).

NOTE: Multiple filters may be prepared and/or analyzed at the same time, but care must be taken to weigh the filters immediately after removal from the desiccator. The collected particulate and, to a certain extent, the filter itself may absorb moisture from the air. Therefore, extended periods of exposure to air between dessication and weighing may lead to inaccurate results.

6. Calculation Procedure

6.1 Calculation of sample volume

6.1.1 Method A. If the sampling rate does not vary more than 0.11 m^3/min (4 ft^3/min), the average sampling rate may be determined by estimating the average value of the deflection on the circular chart for the sampling period and reading the sampling rate corresponding to that deflection from the calibration curve for that unit. The volume of air samples at calibration conditions is calculated by the following equation.

$$V_c = Q \times T \qquad (1)$$

where

V_c = total volume of air sampled at calibration conditions (m^3),

Q = average sampling rate (m^3/min),

T = sampling time (min).

6.1.2 Method B. If the sampling rate varies more than 0.11 m^3/min (4 ft^3/min), the average sampling rate may be obtained by reading the deflection of the circular chart at 2-h intervals for the sampling period and reading the sampling rates corresponding to these deflections off the calibration curve for that unit. The average sampling rate is calculated by:

$$Q = \frac{\sum_{i=1}^{n} Q_i}{n},$$

where

Q = average sampling rate (m^3/min),

Q_i = sampling rate for the ith 2-h interval (m^3/min),

n = number of 2-h intervals.

The volume of air sampled may now be calculated by Equation (1) above.

Method C: After a new filter has been installed in the station, connect a slack tube differential manometer to the differential pressure tap on the sampler motor. Allow motor to run 5 min, then record the reading of the manometer (see instructions for manometer operation). Repeat this procedure at the end of the sampling period and convert these two manometer readings to sampling rates using the appropriate calibration curve. The average sampling rate may now be calculated by:

$$Q = \frac{Q_1 + Q_2}{2} ,$$

where

Q = average sampling rate (m^3/min),

Q_1 = initial sampling rate (m^3/min),

Q_2 = final sampling rate (m^3/min).

The volume of air sampled may now be calculated by Eq. (1) above.

6.2 Pressure and temperature corrections

The total volume of air sampled, V, was determined at calibration temperature and pressure conditions. To convert V to the actual volume of air sampled, corrections for ambient temperature and pressure must be made. The actual volume of air sampled may now be calculated by:

$$V_{actual} = V_c \left(\frac{P_1 \cdot T_2}{T_1 \cdot P_2} \right)^{1/2} ,$$

where

V_c = volume of air sampled at calibration conditions (m^3); (this is the volume calculated in step 6.1),

V_{actual} = volume of air sampled at ambient conditions (m^3),

T_2 = average ambient temperature (K) = °C + 273 (°C average for the day),

P_2 = average ambient pressure (mm Hg); obtained from Shift Supervisor's office),

P_1 = calibration pressure (mm Hg),

T_1 = calibration temperature (K).

6.3 Mass concentration of suspended particulates

Calculate the mass concentration of suspended particulates by the following formula:

$$SP = \frac{(W_f - W_i) \times 10^6}{V_{actual}} , \qquad (5)$$

where

SP = mass concentration of suspended particulates ($\mu g/m^3$),

W_f = final weight of filter (g),

W_i = initial weight of filter (g),

V_{actual} = volume of air sampled at ambient conditions (m^3).

6.4 Record the actual volume of air sampled, V. The sampling time, T, and the mass concentration of suspended particulates, SP, in a suitable log book and report the results.

NOTE: To convert flowmeter readings to cubic meters (m^3) for the above calculations, divide the number of cubic feet (ft^3) by 35.314.

$$m^3 = \frac{ft^3}{35.314}$$

or

$$m^3/min = \frac{ft^3/min}{35.314} .$$

Working Bibliography for Sect. 1.18

Air Sampling Instruments for Evaluation of Atmospheric Contaminants, Fifth Edition, American Conference of Governmental Industrial Hygienists, Cincinnati (1978).

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J. B. Pate and E. C. Tabor, "Analytical Aspects of the Use of Glass Fiber Filters for the Collection and Analysis of Atmospheric Particulate Matter," *Am. Ind. Hyg. Assoc. J.* 23, 144 (1962).

C. D. Robson and K. E. Foster, "Evaluation of Air Particulate Sampling Equipment," *Am. Ind. Hyg. Assoc. J.* 24, 404 (1962).

G. P. Tierney and W. D. Connor, "Hygroscopic Effects on Weight Determinations of Particulates Collected on Glass Fiber Filters," *Am. Ind. Hyg. Assoc. J.* 28, 363 (1967).

Use of 90-Volt Transformers in High Volume Air Sampling, New York State Department of Environmental Conservation Report No. BAQS-45 (1973).

2. TERRESTRIAL SAMPLING

Soil and grass samples are collected annually at the PAM and RAM stations. The grass and soil samples are analyzed for uranium, plutonium, and other radioisotopes using gamma spectroscopy and radiochemical techniques. Various other soil, sediment, and vegetation samples are taken in the environs of Oak Ridge National Laboratory when necessary.

2.1 Procedure for the Collection and Preparation of Soil and Grass Samples for Assaying

Soil samples are taken annually at the PAM and RAM stations and when necessary at other designated areas.

Approximately 15 m from the air monitoring station, four 0.2-m^2 areas are chosen at 90° from each other, along with an area close to the station (Fig. 2.1-1). The grass is cut from each area and combined in a plastic bag. The plastic bag is labeled with the sample's name, date, and location of the air monitoring station. Two soil samples are collected from each area with a circular cutter, 10.5 cm in diameter and adjustable to a depth of 2.5 cm; only the top 2 cm of soil is taken. The soil samples are combined in a plastic bag and labeled with the sample's name, date, and the location of the air-monitoring station.

In the laboratory, the grass sample is finely cut with electric grass cutters, weighed, and dried in an oven for 24 h (or until dry) at 105°C. The grass is reweighed, and the weight of the moisture content is determined. The sample is placed in a Marinelli beaker and delivered to the Analytical Chemistry Division for gamma-spectrometric analysis.

The moisture content of the soil is determined by weighing the sample before and after drying in an oven at 105°C for 24 h. The soil sample is transferred to a blotter box and labeled with the sample's name, date, and the location of the air monitoring station. The soil sample is taken to the grinding room and ground to a fine mesh of 500 μm and less in diameter (Fig. 2.1-2). The following procedure should be followed when grinding soil samples.

1. The following clothing and safety devices should be worn while inside the grinding room:

   1.1 Shoe covers
   1.2 Gloves
   1.3 Lab coat
   1.4 Respirator
   1.5 Safety glasses

Fig. 2.1-1. Soil and grass sampling.

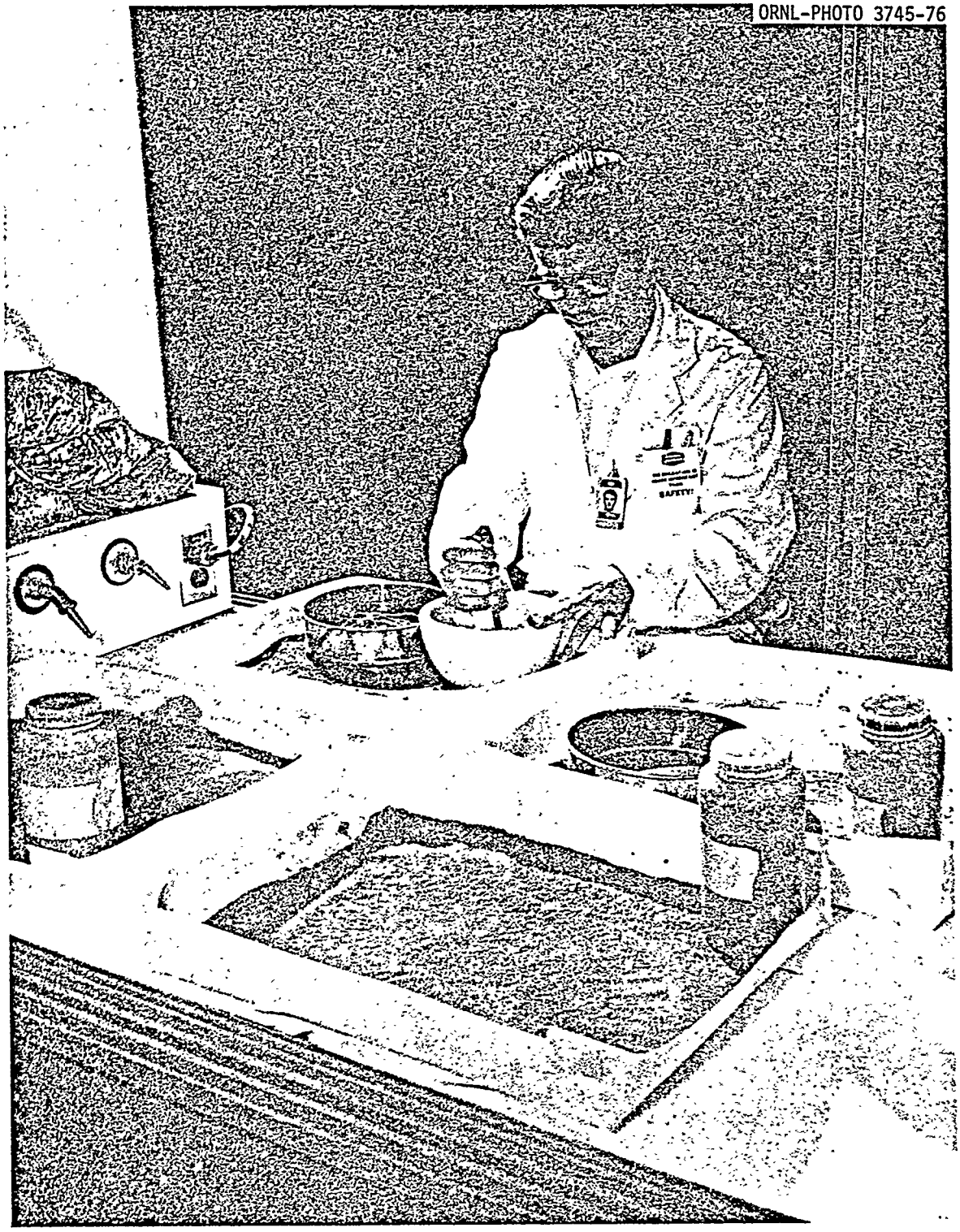

Fig. 2.1-2. Preparation of soil samples.

2. Clean the grinding machine (shown in Fig. 2.1-3) before grinding the soil samples. Open the casing of the machine and inspect the grinder and collection tray for soil particles. It is important that the machine be completely clean to prevent contamination. The machine should be cleaned by using the following procedures.

   2.1 Turn on the ventilation system in the hood.

   2.2 Use a wire brush and a paint brush to remove all particles from the grinder plates and inside walls of the casing. Brush all particles into the collection tray and discard. Use the vacuum hose to clean all remaining particles from the grinder wheels, the inside and outside walls of the casing, and the collection tray.

   2.3 Close the grinder casing and run finely meshed, activity-free, dry sand through the port. This will help loosen hard-to-remove particles.

   2.4 Clean the grinder once again. Also clean the paint and wire brushes thoroughly before using again.

3. Using hooded area, crush all the soil manually inside the blotter paper box. Soil which cannot be crushed will be ground in the machine.

4. Start the machine and slowly feed the soil through the port.

5. Periodically, empty the collection tray containing the ground sample into a clean plastic bag that has been labeled. Remove grass and roots from collection tray and combine with ground grass sample.

6. Clean machine as described previously. Discard excess soil and grass particles into their respective plastic bags.

7. Shake the bag vigorously to ensure mixing of the soil and run soil through the grinder again.

8. Discard the soil into the labeled plastic bag. Open the casing, clean the machine thoroughly, and DISCARD EXCESS PARTICLES.

9. Mix the finely meshed soil by shaking the bag vigorously.

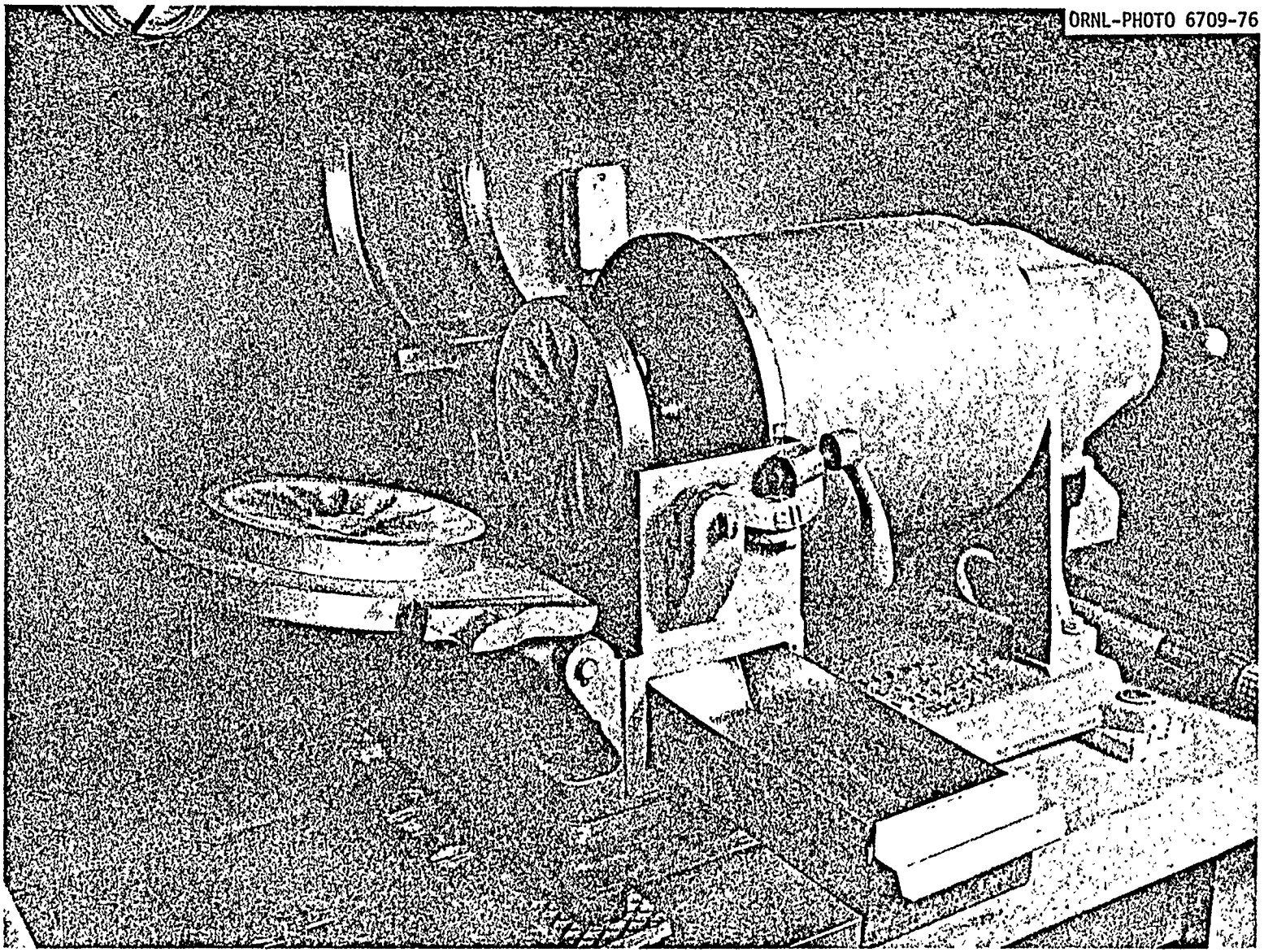

Fig. 2.1-3. Soil grinder.

10. Once packaged, the vial is labeled with the location of sample, date the sample was taken, and date the sample was ground. Clean the outside of the vial with the air hose. The packaged sample is delivered to the Analytical Chemistry Division for gamma-spectrometric analysis.

11. Transfer all the remaining soil sample into a smaller, clean plastic bag and label as in step 10. This sample is stored for future reference.

12. Discard the blotter paper box and old plastic bag.

13. Thoroughly clean the contaminated area. Turn off the ventilation in the hood. Discard gloves, shoe overalls, and respirator (if disposable type).

2.2 Grass Sample Analysis — High-Resolution Gamma-Ray Spectroscopic Method

Annual samples of grass from perimeter and remote air monitoring (PAM and RAM) stations are collected and processed according to the procedure outlined in Sect. 2.1.

1. Sample Preparation

To retain volatile radionuclides in grass, samples are prepared with a minimum of handling. Cordless electric trimming shears are used to cut the grass blades into segments of 2 to 3 cm and placed directly into a 1-liter Marinelli beaker. Sufficient grass is cut to fill the beaker to the 900-ml mark by hand compression. The net weight of "wet" grass is determined to the nearest 0.1 g. The lid is placed on the Marinelli beaker and the entire package is placed into a loose-fitting polyethylene bag for contamination control.

2. Gamma-Ray Spectrometry

The reentrant well in the bottom of the Marinelli beaker is fitted over the end cap of a high-resolution germanium-lithium detector of at least 20% efficiency relative to 1.33 MeV gamma rays on a 7.6- by 7.6-cm NaI(Tl) detector at 25 cm. The detector should have low background and a resolution value of 2.1 keV (or less) full width at half maximum at 1.33 MeV. Spectral data from the detector should be accumulated with at least 2048 channels in a computer-based pulse-height analyzer system. Counting periods of 10,000 to 50,000 s should be employed. Data processing of the gamma-ray spectral information should be performed with a suitable on- or off-line peak search program.

In the present laboratory arrangement, a Nuclear Data, Inc., Model 4420 (ND 4420) computer-analyzer system is used. At the conclusion of the preset counting interval, the gamma-ray spectrum is written onto compatible magnetic tape for IBM 360 processing by means of program MONSTR (see Sect. 2.4). In addition, the operating software (1076-02) of the ND 4420 is used to perform a peak

extraction step yielding net area and energy of the prominent gamma rays in an on-line mode.

3. Calibration

A calibration standard is prepared by diluting a mixed radionuclide solution standard (U.S. National Bureau of Standards or Amersham-Searle, Inc.) in a suitable quantity to fill a 1-liter Marinelli beaker to the 900-ml level. The calibration standard is analyzed in exactly the same manner as the grass samples, yielding a spectrum of gamma-ray energies covering the energy range from 800 to 2000 keV. From the measured counting rates and the certified emission rates, an efficiency curve is constructed. Such a curve consists of a logarithmic plot of efficiency (counts per second divided by emitted gamma rays per second) versus log energy (MeV). The graphic representation may be used directly for determining the efficiency for a given gamma-ray energy, or digital data may be used in determining a quadrate or high-order mathematical expression relating efficiency and energy in applications of program MONSTR.

4. Data Interpretation

Output from program MONSTR should be carefully reviewed and reported based on expected nuclides from previous experiences. In general, grass samples will normally contain beryllium-7, potassium-40, and cesium-137. Other radionuclides may be present at times of global fallout precipitation. Potassium results should be reported only after correction for the 1.46 MeV background contribution.

After completion of the gamma-ray spectrum determination, the grass sample is returned to the Department of Environmental Management for determination of the oven-dried weight. Final compliance results are tabulated in units of becquerels or picocuries per gram of oven-dried material.

5. Quality Control

A known standard long-lived radionuclide source should be processed in the counting system on a regular basis for quality control of the spectrometer system. Currently, this practice consists of

analyzing a radium-226 standard every 2 or 3 days or every 30th spectra, whichever occurs first. The data are processed through the entire system and selected from program MONSTR output in exactly the same fashion as are the unknown samples. The radium-226 content is recorded in a quality control notebook. Deviations greater than ±2% from the label value of standard are reported to the laboratory supervisor for corrective action.

2.3 Soil Sample Analysis — High-Resolution Gamma-Ray Spectroscopic Method

Annual soil samples from perimeter and remote stations are collected and processed according to the procedure outlined in Sect. 2.1.

1. Sample Preparation

A suitable aliquot of the homogenized soil sample is taken to evenly fill a plastic petri dish of 7.0 cm diam and 1.6 cm height. The volume of such a container is about 6.2 cm^3. Nominal soil densities result in sample weights of 70 g, but variations from 50 to 100 g are not uncommon. The net weight of the sample is determined to the nearest 0.1 g. One turn of plastic electrical tape is placed around the edge of the dish to prevent spillage of the contents. The petri dish is placed in a thin polyethylene freezer bag for contamination control before the spectroscopic measurement.

2. Gamma-Ray Spectrometry

The counting sample is placed directly on the end cap of a high-resolution germanium-lithium detector (Fig. 2.3-1) that is described in of Sect. 2.2 "Gamma-Ray Spectrometry."

3. Calibration

A calibration standard consisting of 70 g of New Brunswick Laboratory's uranium standard 42-4 (containing 0.52% for background contributions) is used. Global fallout nuclides (such as cesium-137, antimony-125, and cerium-144) are usually the only fission product nuclides present in most samples.

4. Quality Control

See Sect. 2.2 "Quality Control."

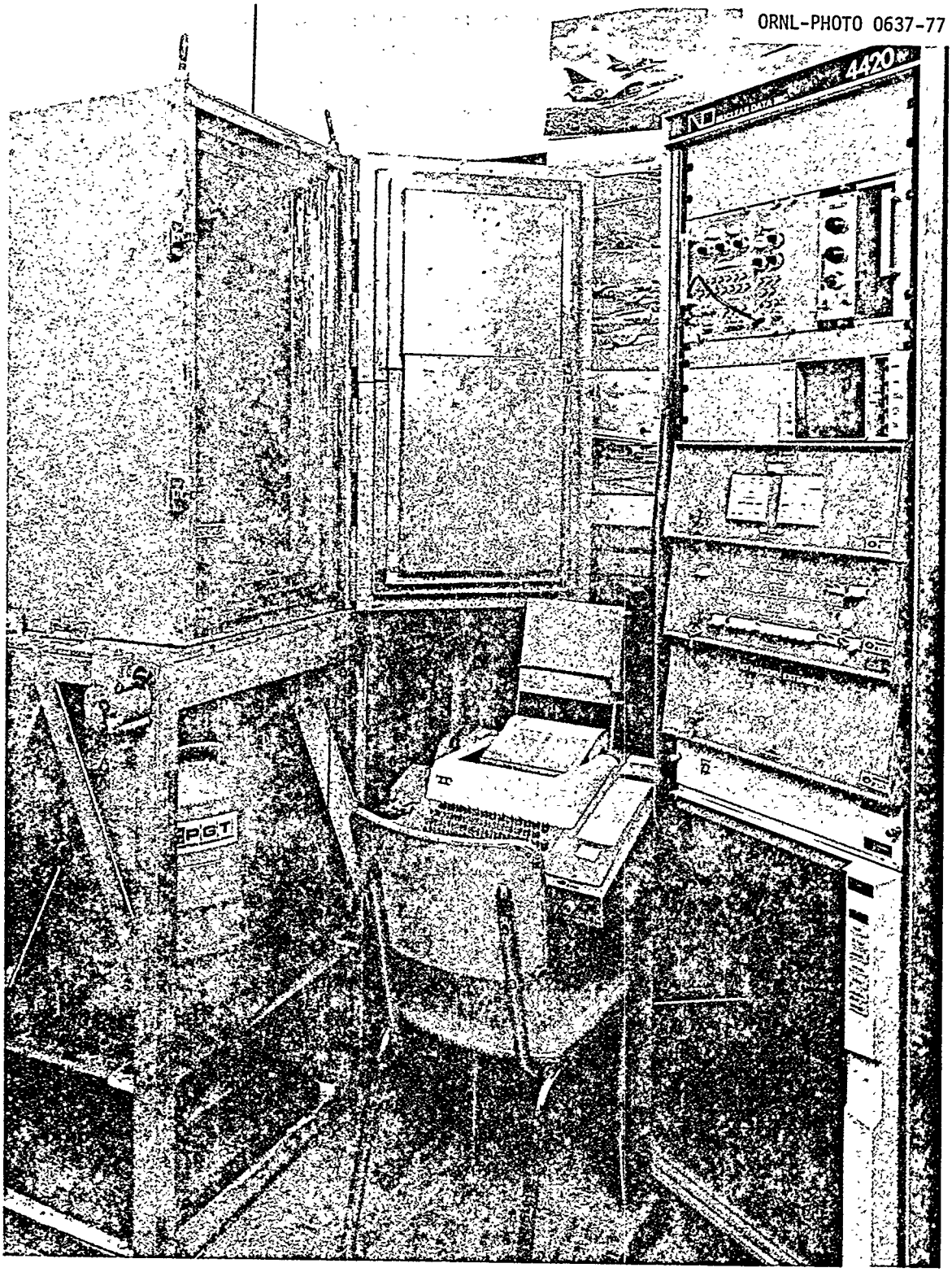

Fig. 2.3-1. Germanium-lithium detector for low-level gamma radiation.

2.4 A General Discussion of the MONSTR Program for Determining Radionuclides with a Germanium-Lithium Detector

MONSTR is a computer program used for the resolution and isotopic identification of any gamma-ray spectra developed by germanium-lithium detection techniques. This includes assaying of low-level environmental samples (which is of primary importance in this manual), as well as neutron-activation and other types of analysis. At ORNL, program MONSTR has been implemented on the IBM 360, DEC 10, and PDP 15 computers.

In the MONSTR program, the accumulated photon spectrum is scanned and each peak's centroid located. (A maximum of 200 photopeaks may be stored for a single spectrum in the IBM 360 computer.) The program then determines peak interferences (such as multiplets), which are defined as two (or more) peaks less than four times full width half maximum in distance apart. A least-squares Gaussian fit, using an iterative technique, is performed on each peak in the spectrum. In cases where interference peaks occur, fitting is accomplished over the entire range rather than for each peak. This method allows for a better fit of the individual peaks in the multiplet. This fitting technique usually converges in four or five iterations. After converging, calculation of each peak's centroid, total area (and error on the area), and full width half maximum is accomplished. The MONSTR program uses an energy calibration curve to determine both the energy and photon disintegration rate for each peak in the spectrum.

The MONSTR program also may be used to identify those radionuclides present (as many as 100 in the IBM 360 computer) in the gamma-ray spectrum. This is accomplished by comparing the individual photopeaks in the sample spectrum with a nuclear data file which contains information on 700 radionuclides and 2500 gamma rays. If the candidate selected for comparison satisfies several tests, it is placed on a list of identified nuclides. One of these tests demands that the peak energy of the candidate must fall within a preselected value of the energies listed in the nuclear data file to qualify as a possible identified radionuclide. It must also pass the other sequential tests before resolving that it is a specifically identified radionuclide. Those candidates that do not pass

all of the tests are listed in an unidentified radionuclide table. After the candidate list has been exhausted, the disintegration rate and concentration in microcuries (becquerels) for each isotope are computed. When the isotope has two or more gamma rays associated with it, the average and percentage standard deviation is tabulated. A maximum of five gamma rays may be used for this computation.

Other options are also available with the MONSTR program. A LIMIT command allows for the determination of the minimum detectable activity of preselected radionuclides, even if the radionuclides are not present in the sample. Also, STRIP and PLOT commands are available which perform the tasks implied by their names. The reader is strongly encouraged to review the bibliography listed below for detailed discussion of the MONSTR program.

Working Bibliography for Sect. 2.4

J. F. Emery and F. F. Dyer, "Multielemental Determination in Environmental NAA Using MONSTR," *Proceedings of the Second International Conference on Nuclear Methods in Environmental Research*, CONF-740701, p. 123, July 1974.

RSIC Data Library Collection, DECAYGAM: Radionuclide Gamma-Ray Energy and Intensity Compilation, ORNL-DLC-19.

2.5 Radiochemical Method for Determining Plutonium in Soil and Sediments

(performed by Analytical Chemistry Division Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

This method is applicable to the determination of plutonium in soils and sediments.

2. Summary of Method

2.1 A known quantity of plutonium-242 tracer, which is used as an internal standard, is added to the sample leached by hot nitric acid and hot nitric acid–hydrogen peroxide. Plutonium is adjusted to Pu^{+4}, adsorbed on anion exchange resin, reduced to Pu^{+3}, and selectively eluted from the resin. Subsequently, plutonium is carried on praseodymium hydroxide, dissolved and oxidized to Pu^{+4}, and extracted with thenoyltrifluoroacetone-xylene. The organic extract is evaporated on a stainless steel disk, and the plutonium is determined by alpha spectrometry.

2.2 The lowest reported concentration is 1.48×10^{-4} Bq/g (4×10^{-3} pCi/g) for 10-g samples.

3. Sample Handling and Preservation

3.1 The samples are oven dried at 105°C to a constant weight, pulverized, and screened to 100-mesh particle size.

3.2 The dried and screened sample material is stored in airtight glass or plastic containers.

4. Interferences

4.1 Samples that are of a refractory nature, such as test-site materials, are not apt to release plutonium in the leaching process; therefore, more rigorous treatment is recommended for decomposition of these samples.

4.2 Plutonium-240 cannot be distinguished from plutonium-239 by alpha pulse-height analysis; however, alpha pulse-height analysis eliminates most other alpha interferences.

5. Apparatus

5.1 Drying oven

5.2 Muffle furnace

5.3 Hot plate with magnetic stirrer

5.4 Centrifuge

5.5 Vortex mixer

5.6 Extraction vials, 50-ml with plastic-lined screw caps

5.7 Screens, 40- and 100-mesh

5.8 Transfer pipettes

5.9 Lab glassware

5.9.1 Beakers, 250-ml size and 500-ml tall-form

5.9.2 Centrifuge tubes, 50-ml glass and 100-ml plastic

5.9.3 Glass ion-exchange column, 8 mm ID by 25 cm long, fitted with a stopcock and reservoir

5.10 Stainless steel disks

5.11 Multichannel analyzer system with silicon surface-barrier detector(s)

5.12 Analytical balance

5.13 Magnetic stirring bar, Teflon coated, 3.8 cm (1.5 in.) long

6. Reagents

6.1 Nitric acid (HNO_3), concentrated

6.2 Nitric acid (HNO_3), 8M: Add 500 ml of concd HNO_3 to 500 ml of water.

6.3 Ammonium hydroxide (NH_4OH), concentrated

6.4 Plutonium-242 tracer solution: Dilute an NBS-certified (or equivalent) solution of plutonium-242 to a concentration of 10 dis min^{-1} ml^{-1} with 2M HNO_3 and store in glass.

6.5 Nitric acid (HNO_3), 1M: Add 62.5 ml of concd HNO_3 to 500 ml of water and dilute to 1 liter with water.

6.6 Sodium nitrite ($NaNO_2$), crystals

6.7 $NaNO_2$ solution, 3M: Dissolve 10.4 g of $NaNO_2$ in water and dilute to 50 ml with water. Make fresh daily.

6.8 Thenoyltrifluoroacetone (TTA)-xylene solution, 0.5M TTA: Dissolve 111 g of $SC_4H_3COCH_2COCF_3$ (TTA) in xylene and dilute to 1 liter with xylene.

6.9 Ferric nitrate solution, 0.1M: Dissolve 40.4 g of ferric nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$] in water and dilute to 1 liter with water.

6.10 Hydroxylamine-hydrochloride solution, 5M: Dissolve 347.5 g of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in water and dilute to 1 liter with water.

6.11 Hydrochloric acid–hydroxylamine hydrochloride solution, 0.5M HCl-0.05M $NH_2OH \cdot HCl$: Add 42 ml of concd HCl and 10 ml of 5M $NH_2OH \cdot HCl$ to 500 ml of water and dilute to 1 liter with water.

6.12 Hydrochloric acid (HCl), concentrated

6.13 Praseodymium carrier solution: Dissolve 12.82 g of praseodynium nitrate dihydrate [$Pr(NO_3)_3 \cdot 2H_2O$] in 500 ml of water and dilute to 1 liter with water.

6.14 Anion exchange resin: Dowex 1-X4 (50-100 mesh, chloride form) or equivalent

6.15 Hydrochloric acid (HCl), 8M: Add 666 ml of concd HCl to 334 ml of water.

6.16 Hydrogen peroxide (H_2O_2), 30% solution

7. Procedure

7.1 Transfer a measured weight (5 to 10 g) of the 100-mesh sample to a 500-ml tall-form beaker. If the sample shows signs of containing organic matter, ash in a muffle furnace at 500°C for several hours before continuing.

7.2 Slowly add 50 to 75 ml of 8M HNO_3 and allow sufficient time for any foaming to subside.

7.3 Add 1 ml of 10 dis min^{-1} ml^{-1} plutonium-242 tracer solution.

7.4 Carefully introduce the magnetic stirring bar, place the beaker on the hot plate, and digest the sample with stirring at 90 to 95°C for 1 h.

7.5 Remove the beaker from the hot plate and transfer the sample solution to a 100-ml plastic centrifuge tube.

7.6 Centrifuge for 10 min at 1500 rpm.

7.7 Decant the supernatant liquid into a 250-ml beaker and retain.

7.8 Rinse the residue from the centrifuge tube into the original 500-ml beaker with 50 to 75 ml of 8M HNO_3.

7.9 Return the beaker to the hot plate at 90 to 95°C. Digest the sample, adding a few drops of 30% H_2O_2 intermittently for a total of 5 to 10 ml, while stirring for 1 h.

7.10 Repeat steps 7.5 through 7.7.

7.11 Repeat step 7.8 using 25 ml of 1M HNO_3.

7.12 Repeat steps 7.9 and 7.10 and discard the residue.

7.13 Add 250 mg of $NaNO_2$ crystals to the 250-ml beaker, place on a hot plate, bring to a boil rapidly, immediately remove from heat, and allow the sample to digest for 20 min to adjust the valence of plutonium to Pu^{+4}.

7.14 While the sample is digesting, prepare a resin column as follows:

7.14.1 Place a glass-wool plug in the bottom of the column described in step 5.9.3.

7.14.2 Slurry the resin (see step 6.14) with water and immediately discard the fines by decanting. Repeat as necessary until fines are removed.

7.14.3 Transfer 4 ml of resin to the column with water. Prevent any channeling by maintaining the solution level above the resin in the stopcock.

7.14.4 Place a glass-wool plug on top of the resin.

7.14.5 Convert the resin to the nitrate form by passing several column volumes of 8M HNO_3 through the column until the resin is free of chloride ions.

7.15 Transfer the sample solution, which should be at room temperature, to the prepared resin column and allow it to flow through the column at a rate of 2 ml/min. Discard the effluent solution.

7.16 Rinse the beaker with 25 ml of 8M HNO_3 and transfer the rinse to the column. Allow the 8M HNO_3 rinse to flow through the column at a rate of 2 ml/min. Discard the effluent solution.

7.17 Rinse the beaker with 25 ml of 8M HCl and transfer the rinse to the column. Allow the 8M HCl rinse to flow through the column at a rate of 2 ml/min. Discard the effluent solution.

7.18 Add one drop of 0.1M $Fe(NO_3)_3$ and 1 ml of 5M $NH_2OH \cdot HCl$ to the column. Open the stopcock and allow the solution to drain to the top of the resin bed, then stop the flow. Discard the effluent solution.

7.19 Add 4 ml of 0.5M HCl-0.05M $NH_2OH \cdot HCl$ solution. Place a 50-ml glass centrifuge tube under the column. Allow 3 ml of solution to drain into the tube and close the stopcock.

7.20 Allow 20 min digestion time for reduction of the plutonium to Pu^{+3}.

7.21 Add 25 ml of 0.5M HCl-0.05M $NH_2OH \cdot HCl$ solution. Pass the solution through the column at a flow rate of 2 ml/min into the 50-ml tube.

7.22 Add 1 ml of praseodymium carrier to the sample solution in the 50-ml tube and mix thoroughly.

7.23 Add concd NH_4OH and adjust to pH of 9 while stirring. Allow 15 min digestion time.

7.24 Centrifuge for 10 min at 1500 rpm and discard the supernatant solution.

7.25 Wash the precipitate with water, centrifuge, and discard the water wash solution.

7.26 Dissolve the precipitate in six drops of concd HNO_3 and transfer the dissolved sample to a 50-ml extraction vial with 5 ml of 1M HNO_3. Add ten drops of 3M $NaNO_2$, mix well, and allow 20 min digestion time for plutonium to oxidize to Pu^{+4}.

7.27 Add 1 ml of 0.5M TTA-xylene solution and extract on a Vortex mixer for 10 min.

7.28 Centrifuge for 2 min to separate the phases. Discard the aqueous phase.

7.29 Scrub the TTA extract with 5 ml of 1M HNO_3. Centrifuge and discard the aqueous phase.

7.30 Transfer the TTA to a stainless steel disk and place on a hot plate set at 150°C. Allow the TTA to dry thoroughly.

7.31 Flame the stainless steel disk to a red heat.

7.32 Measure the alpha activities by pulsing with a silicon surface-barrier detector coupled to a multichannel analyzer.

8. Calculations

$$^{238}Pu = ACM/DE \text{ , Bq/g ,}$$

$$^{239}Pu = BCM/DE \text{ , Bq/g ,}$$

where

A = net integrated counts of ^{238}Pu from pulse analysis,

B = net integrated counts of ^{239}Pu from pulse analysis,

C = dis/min of ^{242}Pu added,

D = net integrated counts of ^{242}Pu from pulse analysis,

E = weight of sample in grams,

M = conversion factor from dis/min to Bq: 1 Bq = 60 dis/min.

9. Precision and Accuracy

The precision is estimated to be ±20%. The accuracy has not been established.

Working Bibliography for Sect. 2.5

George H. Coleman, *The Radiochemistry of Plutonium*, National Academy of Sciences — National Research Council, NAS-NS 3058, Sept. 1, 1965.

John H. Harley, *EML Procedures Manual*, HASL-300, current edition.

Frederic B. Johns (ed.), *Handbook of Radiochemical Analytical Methods*, EPA-680/4-75-001, February 1975.

2.6 Radiochemical Method for Determining Uranium Isotopes in Soils and Sediments

(performed by Analytical Chemistry Division Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

This method is applicable to the determination of uranium isotopes in soil and sediment samples.

2. Summary of Method

2.1 A known quantity of uranium-232 tracer, used as an internal standard, is added to the sample that is leached with a hot nitric acid and hot nitric acid-hydrogen peroxide treatment. The leaching solution is passed through an anion exchange resin to adsorb plutonium and thorium, leaving purified uranium in the effluent solution. The uranium is further purified by repeated extractions with methyl isobutyl ketone (hexone). The final hexone extract is dried on a stainless steel disk and counted on a multichannel analyzer system using a silicon surface-barrier detector to determine the uranium concentration.

2.2 The lowest reported concentration is 1.48×10^{-4} Bq/g (4×10^{-3} pCi/g) for 10-g samples.

3. Sample Handling and Preservation

3.1 The samples are oven dried at 105°C to a constant weight, pulverized, screened to 100-mesh particle size, and thoroughly blended.

3.2 The prepared sample materials are stored in airtight glass or plastic containers.

4. Interferences

4.1 Indigenous uranium is not likely to be released in the leaching process; therefore, more rigorous methods should be used for its determination.

4.2 Iron in milligrams per gram concentrations tends to follow uranium throughout the chemistry and causes serious degradation of alpha measurements.

4.3 Uranium-234 cannot be distinguished easily from uranium-233 by alpha pulse-height analysis.

5. Apparatus

5.1 Drying oven

5.2 Muffle furnace

5.3 Hot plate with magnetic stirrer

5.4 Centrifuge

5.5 Vortex mixer

5.6 Extraction vials, 50-ml with plastic-lined screw caps

5.7 Screens, 40- and 100-mesh

5.8 Transfer pipettes

5.9 Lab glassware

5.9.1 Beakers, 250-ml size and 500-ml tall-form

5.9.2 Centrifuge tubes, 50-ml glass and 100-ml plastic

5.9.3 Glass ion exchange column, 8 mm ID by 25 cm long, fitted with a stopcock and reservoir

5.10 Stainless steel disks

5.11 Multichannel analyzer system with silicon surface-barrier detector(s)

5.12 Analytical balance

5.13 Magnetic stirring bar, Teflon coated, 3.8 cm (1.5 in.) long

6. Reagents

6.1 Nitric acid (HNO_3), concentrated

6.2 Nitric acid (HNO_3), 8M: Add 500 ml of concd HNO_3 to 500 ml of water.

6.3 Aluminum nitrate solution, 2.8M: Dissolve 1050 g of aluminum nitrate nonahydrate [$Al(NO_3)_3 \cdot 9H_2O$] in a minimum of water with heat. Cautiously add 100 ml of concd NH_4OH with stirring. Continue heating and stirring until all of the precipitate dissolves, and then dilute to 1 liter with water.

6.4 Sodium nitrite ($NaNO_2$), crystals

6.5 Methyl isobutyl ketone (hexone)

6.6 Potassium bromate ($KBrO_3$), crystals

6.7 Uranium-232 tracer solution: Dilute a stock solution of uranium-232 to a concentration of 10 dis min^{-1} ml^{-1}.

6.8 Anion exchange resin: Dowex 1-X4 (50-100 mesh, chloride form) or equivalent

6.9 Hydrogen peroxide (H_2O_2), 30% solution

7. Procedure

7.1 Transfer a measured weight (5 to 10 g) of the 100-mesh sample to a 500-ml tall-form beaker. If the sample shows signs of containing organic matter, ash in a muffle furnace at 500°C for several hours before continuing.

7.2 Slowly add 50 to 75 ml of 8M HNO_3 and allow sufficient time for any foaming to subside.

7.3 Add 1 ml of 10 dis min^{-1} ml^{-1} uranium-232 tracer solution.

7.4 Carefully introduce the magnetic stirring bar, place on the hot plate, and digest, with stirring, at 90 to 95°C for 1 h.

7.5 Remove from the hot plate and transfer the sample solution to a 100-ml plastic centrifuge tube.

7.6 Centrifuge for 10 min at 1500 rpm.

7.7 Decant the supernatant liquid into a 250-ml beaker and retain.

7.8 Rinse the residue from the centrifuge tube into the original 500-ml beaker with 50 to 75 ml of 8M HNO_3.

7.9 Return to the hot plate and digest with stirring at 90 to 95°C for 1 h while adding a few drops of 30% H_2O_2 intermittently for a total of 5 to 10 ml.

7.10 Repeat steps 7.5 through 7.7.

7.11 Repeat steps 7.8 using 25 ml of 1M HNO_3.

7.12 Repeat steps 7.9 and 7.10 and discard the residue.

7.13 Add 250 mg of $NaNO_2$ crystals, place on hot plate, bring to a boil rapidly, immediately remove from heat, and allow the sample to digest for 20 min.

7.14 While the sample is digesting, prepare a resin column as follows:

7.14.1 Place a glass-wool plug in the bottom of the column described in step 5.9.3.

7.14.2 Slurry the resin (see step 6.8) with water and immediately discard the fines by decanting. Repeat as necessary until fines are removed.

7.14.3 Transfer 4 ml of resin to the column with water. Prevent any channeling by maintaining the solution level above the resin by use of the stopcock.

7.14.4 Place a glass-wool plug on top of the resin.

7.14.5 Convert the resin to the nitrate form by passing several column volumes of 8M HNO_3 through the column until the resin is free of chloride ions.

7.15 Transfer the sample solution, which should be at room temperature, to the prepared resin column.

7.16 Place a 250-ml beaker beneath the column and allow the sample solution to drain into the beaker at a flow rate of 2 ml/min.

7.17 Rinse the beaker with 25 ml of 8M HNO_3 and transfer the rinse to the column.

7.18 Allow the rinse to drain into the beaker also.

7.19 Place the beaker containing the column effluent on a hot plate to dry.

7.20 Dissolve the residue in 10 ml of $Al(NO_3)_3$ solution and transfer to an extraction vial using a minimum of $Al(NO_3)_3$ to rinse the beaker.

7.21 Add an equal volume of hexone and extract on a Vortex mixer for 10 min.

7.22 Centrifuge for 2 min to separate the phases and discard the aqueous phase.

7.23 Add an equal volume of water and back-extract into the water on a Vortex mixer for 10 min.

7.24 Centrifuge for 2 min to separate the phases.

7.25 Transfer the aqueous phase to a 100-ml beaker.

7.26 Repeat steps 7.23, 7.24, and 7.25.

7.27 Place the beaker containing the water strip solution on a hot plate to dry.

7.28 Add enough 8M HNO_3 to moisten the residue.

7.29 Add 10 to 20 mg of $KBrO_3$ crystals and digest for 10 min.

7.30 Dissolve and transfer the residue to an extraction vial with 5 ml of $Al(NO_3)_3$ solution.

7.31 Repeat step 7.21 using 1 ml of hexone; repeat step 7.22.

7.32 Transfer the entire hexone extract, by drops, to a stainless steel disk placed on a hot plate set at 100°C.

7.33 Flame the disk to a red heat.

7.34 Measure the uranium alpha activities by pulsing with a silicon surface-barrier detector and multichannel analyzer.

8. Calculations

$$^{238}U = AEM/DV \text{ , Bq/g ,}$$
$$^{235}U = BEM/DV \text{ , Bq/g ,}$$
$$^{234}U = CEM/DV \text{ , Bq/g ,}$$

where

A = net integrated counts of ^{238}U from pulse analysis,
B = net integrated counts of ^{235}U from pulse analysis,
C = net integrated counts of ^{234}U from pulse analysis,
D = net integrated counts of ^{232}U from pulse analysis,
E = dis/min of ^{232}U tracer added,
V = weight of sample in grams,
M = conversion factor from dis/min to Bq: 1 Bq = 60 dis/min.

9. Precision and Accuracy

9.1 The precision is estimated to be ±15%.

9.2 The accuracy has not been established; however, no significant bias is indicated.

Working Bibliography for Sect. 2.6

J. E. Grindler, *The Radiochemistry of Uranium*, NAS-NS 3050, March 1962.

F. B. Johns (ed.), *Handbook of Radiochemical Methods*, EPA-680/4-75-001, February 1975.

2.7 Radiochemical Method for Determining Strontium-90 in Soils and Sediments

(performed by Analytical Chemistry Division Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

This method is applicable to the determination of strontium-90 in soil and sediment samples.

2. Summary of Method

2.1 A known weight of strontium carrier is added to the sample that is leached with hot nitric acid and hot nitric acid–hydrogen peroxide treatment. The leachate is reduced in volume and the strontium is separated from calcium, magnesium, and rare earths by nitrate precipitation followed by acetone washes. Further purification is accomplished by removing yttrium and other impurities with hydroxide scavenging and by removing barium and radium as the chromates; final purification is made by precipitation of strontium as the oxalate, which is mounted for beta counting and counted on a low-background beta counter.

2.2 The lowest reported concentration is 7.4×10^{-3} Bq/g (0.2 pCi/g) for 10-g samples.

3. Sample Handling and Preservation

3.1 The samples are oven dried at 105°C to a constant weight, pulverized, screened to 100-mesh particle size, and thoroughly blended.

3.2 The prepared sample material is stored in airtight glass or plastic containers.

4. Interferences

4.1 Samples that are of a refractory nature, such as test-site materials, are not apt to release strontium in the leaching process; therefore, more rigorous treatment is recommended for decomposition of these samples.

4.2 Strontium-89, when present in the sample, interferes with the beta counting of strontium-90. The presence of strontium-89 can be ascertained by absorption studies; the interferences of strontium-89 can be circumvented by indirect determination of strontium-90 via the yttrium-90 daughter after adequate ingrowth.

4.3 Strontium-90 is self-absorbing; therefore the counting efficiency varies with the amounts of solids which are counted on the mounts.

5. Apparatus

5.1 Drying oven
5.2 Muffle furnace
5.3 Hot plate with magnetic stirrer
5.4 Centrifuge
5.5 Screens, 40- and 100-mesh
5.6 Analytical balance
5.7 Pulverizer
5.8 Magnetic stirring bar, Teflon coated, 3.8 cm (1.5 in.) long
5.9 Lab glassware
  5.9.1 Beakers, 250-ml size and 500-ml tall-form
  5.9.2 Centrifuge tubes, 50-ml glass and 100-ml plastic
  5.9.3 Fritted-glass filter crucibles
5.10 Filter flask and funnel
5.11 Filter paper, No. 541 Whatman (11 cm)
5.12 Filter paper, No. 1 Whatman (18 mm)
5.13 Ice bath
5.14 Desiccator
5.15 Low-background beta counter

6. Reagents

6.1 Nitric acid (HNO_3), fuming
6.2 Nitric acid (HNO_3), concentrated
6.3 Nitric acid (HNO_3), 8M: Add 500 ml of concd HNO_3 to 500 ml of water.

6.4 Nitric acid (HNO_3), 6M: Add 375 ml of concd HNO_3 to 500 ml of water and dilute to 1 liter with water.

6.5 Ammonium hydroxide (NH_4OH), concentrated

6.6 Acetic acid, 6M: Add 340 ml of glacial acetic acid (CH_3COOH) to 500 ml of water and dilute to 1 liter with water.

6.7 Ammonium acetate solution, 6M: Dissolve 462 g of ammonium acetate ($NH_4C_2H_3O_2$) in 500 ml of water and dilute to 1 liter with water.

6.8 Ammonium oxalate solution, saturated: Add 200 g of ammonium oxalate monohydrate [$(NH_4)_2C_2O_4 \cdot H_2O$] to 500 ml of water in a 1-liter container, dilute to 1 liter with water, mix thoroughly, and let stand overnight before using.

6.9 Sodium chromate solution, 1.5M: Dissolve 176 g of sodium chromate quadrihydrate ($Na_2CrO_4 \cdot 4H_2O$) in water and dilute to 500 ml with water.

6.10 Barium carrier solution, 10 mg Ba/ml: Dissolve 19.0 g of barium nitrate [$Ba(NO_3)_2$] in water and dilute to 1 liter with water.

6.11 Acetone (C_3H_6O)

6.12 Hydrogen peroxide (H_2O_2), 30% solution

6.13 Phenolphthalein indicator solution, 5%: Dissolve 5 g of phenolphthalein ($C_{20}H_{14}O_4$) in 50 ml of 95% ethyl alcohol (C_2H_5OH) and dilute to 100 ml with water.

6.14 Ethyl alcohol (C_2H_5OH), 95%

6.15 Diethyl ether ($C_2H_5OC_2H_5$), anhydrous

6.16 Ammonium hydroxide (NH_4OH), concentrated

6.17 Strontium carrier solution: Dissolve 27.3 g of strontium nitrate [$Sr(NO_3)_2$] in a minimum of HNO_3 and dilute to 1 liter with water.

6.17.1 Standardization of strontium carrier: Pipette 5.00 ml of strontium carrier solution into a 100-ml beaker and add 30 ml of water. Adjust the pH to 9.0 with concd NH_4OH, add 10 ml of saturated $(NH_4)_2C_2O_4$ solution, and heat to near boiling while stirring. Cool to room temperature and quantitatively transfer the precipitate

to a previously tared filter crucible with hot water. Wash the precipitate several times with hot water, three times with 10-ml portions of ethyl alcohol, and two times with 10-ml portions of diethyl ether. Desiccate the crucible and precipitate under vacuum to a constant weight. The net weight of the precipitate is the weight of strontium oxalate monohydrate ($SrC_2O_4 \cdot H_2O$) in 5.00 ml of the strontium carrier solution.

6.18 Ferric nitrate solution, 0.1M: Dissolve 40.4 g of ferric nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$] in water and dilute to 1 liter with water.

7. Procedure

7.1 Transfer a measured weight (5 to 10 g) of 100-mesh sample to a 500-ml tall-form beaker. If the sample shows signs of containing organic matter, ash in a muffle furnace at 500°C for several hours before continuing.

7.2 Slowly add 50 to 75 ml of 8M HNO_3 and allow sufficient time for any foaming to subside.

7.3 Add 1 ml strontium carrier solution.

7.4 Carefully introduce the magnetic stirring bar, place on the hot plate, and digest with stirring at 90 to 95°C for 1 h.

7.5 Remove from the hot plate and transfer the sample solution to a 100-ml plastic centrifuge tube.

7.6 Centrifuge for 10 min at 1500 rpm.

7.7 Decant the supernatant liquid into a 250-ml beaker and retain.

7.8 Rinse the residue from the centrifuge tube into the original 500-ml beaker with 50 to 75 ml of 8M HNO_3.

7.9 Return to the hot plate and digest with stirring at 90 to 95°C for 1 h with the addition of a few drops of 30% H_2O_2 intermittently for a total of 5 to 10 ml.

7.10 Repeat steps 7.5 through 7.7.

7.11 Repeat step 7.8 using 25 ml of 1M HNO_3.

7.12 Repeat steps 7.9 and 7.10 and discard the residue.

7.13 Place the 250-ml beaker containing the leach solution on a hot plate and reduce the volume to 15 ml.

7.14 Transfer the sample solution to a 50-ml glass centrifuge tube rinsing the 250-ml beaker with a minimum of fuming HNO_3.

7.15 Add fuming HNO_3 to give a total volume of 40 ml.

7.16 Place the 50-ml tube in an ice bath and digest the sample with frequent stirring for 30 min to precipitate the nitrates.

7.17 Remove the tube from the ice bath and centrifuge for 10 min at 1500 rpm. Decant the supernatant solution into a large volume of water and discard.

7.18 Dissolve the precipitate in a minimum of water.

7.19 Add 15 ml of fuming HNO_3 and 15 ml of concd HNO_3.

7.20 Repeat steps 7.16 and 7.17.

7.21 Drain the tube completely, leaving no trace of HNO_3, as a precaution against any adverse reaction with the acetone wash which follows.

7.22 Add 30 ml of acetone and wash the precipitate thoroughly with stirring.

7.23 Centrifuge for 5 min at 1500 rpm and decant the acetone wash into a clearly marked organic-waste container.

7.24 Repeat steps 7.18, 7.19, 7.16, and 7.17.

7.25 Repeat steps 7.21, 7.22, and 7.23.

7.26 Dissolve the precipitate in 10 ml of water.

7.27 Add two drops of phenolphthalein indicator solution and 0.5 ml of 0.1M $Fe(NO_3)_3$ solution.

7.28 Add concd NH_4OH dropwise with stirring until the phenolphthalein end point is reached, then add five more drops.

7.29 Centrifuge for 5 min at 1500 rpm.

7.30 Filter the supernatant solution through No. 541 filter paper into another 50-ml glass centrifuge tube; discard the precipitate. Record the time at which the filtering is done as the separation time of strontium-90 from yttrium-90. Wash the filter with 3 ml of water.

7.31 Neutralize the solution with 6M HNO_3; then add 1 ml of 6M acetic acid, 2 ml of 6M ammonium acetate, and 1 ml of barium carrier.

7.32 Heat the solution to near boiling, then add 1.5M Na_2CrO_4 solution dropwise with stirring to precipitate barium chromate. Chill in an ice bath and stir to complete the precipitation. Check for complete precipitation of barium by adding a few more drops of Na_2CrO_4.

7.33 Centrifuge for 5 min at 1500 rpm.

7.34 Filter the supernatant solution through No. 541 filter paper into another 50-ml glass centrifuge tube and wash the filter with 3 ml of water. Discard the precipitate.

7.35 Add 2 ml of concd NH_4OH to the solution and heat to boiling.

7.36 Add 5 ml of saturated ammonium oxalate solution while stirring to precipitate the strontium oxalate.

7.37 Chill in an ice bath and continue to stir to complete the precipitation.

7.38 Centrifuge for 5 min at 1500 rpm and discard the supernatant solution.

7.39 Place a tared 18-mm filter paper in the filtering funnel and wet with water, using vacuum on the filtering flask.

7.40 Transfer the precipitate onto the filter with hot water; then wash with two 10-ml portions of hot water, three 5-ml portions of 95% ethyl alcohol, and two 5-ml portions of diethyl ether.

7.41 Weigh the filter paper and precipitate, determine the chemical recovery, and mount for beta counting.

7.42 Count the sample amount without delay on a low-background beta counter.

8. Calculations

$$^{90}Sr = ABM/DV \ , \quad Bq/g \ ,$$

where

A = net counts per min of purified ^{90}Sr,

B = efficiency factor for ^{90}Sr, including self-adsorption correction,

D = fraction of strontium carrier recovered,

V = weight of sample in grams,

M = conversion factor from dis/min to Bq: 1 Bq = 60 dis/min.

9. Precision and Accuracy

The precision at the 95% confidence level is ±12%. The method exhibits a positive bias of 25% when applied to controls of known strontium-90 concentration.

Working Bibliography for Sect. 2.7

M. A. Franson (ed.), *Standard Methods for Examination of Water and Waste Water*, 14th ed., 1976.

R. B. Hahn and C. P. Straub, "Determination of Radioactive Strontium and Barium in Water," *J. Am. Works Assoc.*, 47, No. 4, p. 335 (1955).

J. Kooi, "Quantitative Determination of Strontium-89 and Strontium-90 in Water," *Anal. Chem.*, 30, p. 532 (1958).

3. BIOLOGICAL SAMPLING

The biological sampling program is centered around the capture of fish from the Clinch River and its tributaries and the collection of milk samples (local and remote) and small road-killed animals. Fish belonging to the same species are ashed and prepared for analysis. The fish samples are analyzed by atomic absorption for mercury and by gamma spectrometry and radiochemical techniques for radionuclides which may contribute to the radiation dose in man. Milk samples are collected weekly at the local milk stations and once during a 5-week interval at the remote milk stations. The milk samples are analyzed for iodine-131 and strontium-90. Local produce is also collected on an annual basis for analysis of radioactivity and trace metal content. The road-killed animals are analyzed for gamma activity. The procedures in this section are also applicable to other biological samples.

3.1 Procedure for Handling Biological Samples

1. Some biological samples (e.g., road-killed deer) are delivered to members of the Department of Environmental Management Section by staff members from the Environmental Science Division (ESD). Technicians from the DEM also collect other necessary samples not acquired by the ESD personnel.

2. The samples are assigned identification numbers and are logged in with the following information:
   - 2.1 Species of sample
   - 2.2 Weight
   - 2.3 Location where sample was collected
   - 2.4 Date sample was found
   - 2.5 Name of persons delivering and receiving sample
   - 2.6 The alpha and beta-gamma direct radiation reading and smear reading

3. Samples are double-bagged in plastic bags, sealed, and stored in the freezer.

4. Once counting time has been scheduled, the samples are removed from the freezer, placed in a third plastic bag or Marinelli beaker, and transferred to the Analytical Chemistry Counting Facilities.

5. After the completion of counting, the samples are returned to the DEM and replaced in the freezer for further evaluation.

3.2 Preparation of Biological Samples for Radionuclides and Elemental Evaluations (Dry-Ashing)

1. Samples that are dry-ashed for radionuclide evaluation include fish and local and commercial food products.

2. Fish samples are collected from the Clinch River and several of its tributaries. The collection locations include:
   - 2.1 Above Melton Hill Dam at Clinch River Mile CRM 25.0.
   - 2.2 The junction of White Oak Creek and Clinch River, CRM 20.8.
   - 2.3 The junction of Poplar Creek and Clinch River, CRM 12.0.
   - 2.4 Centers Ferry at Kingston, Tennessee, CRM 5.0.

To collect fish samples, an electrical probe (Fig. 3.2-1) is inserted into the water and a 60-A current is applied. An electrical current is established between the probe and the bottom of the boat, thus temporarily immobilizing the fish. The fish are captured in a net (Fig. 3.2-2) and separated according to species (bass, crappie, blue gill, carp, and shad). Ten fish of each species are collected at each location. The fish are placed in plastic bags which are labeled with date, location, and species. The excess fish are released. The fish samples are returned to the laboratory and frozen, if not prepared on the day of collection.

When the fish are prepared for analysis, they should be thawed, weighed separately, and combined according to species and location of collection. If possible, ten fish of the same species and locations are scaled, eviscerated, deboned, decapitated, and combined. In each of these operations, the anatomical parts are placed in a separate plastic bag, frozen, and stored. The combined muscles are weighed, placed in a weighed Pyrex beaker, and labeled.

3. Food products (Fig. 3.2-3 and 3.2-4) are purchased from commercial supermarkets in the Knoxville/Oak Ridge area for background levels and from local residents for determining the impact of the facilities on local produce. The sample date and site of collection are recorded. Meats, vegetables, and other food samples which might spoil if not prepared immediately, are frozen.

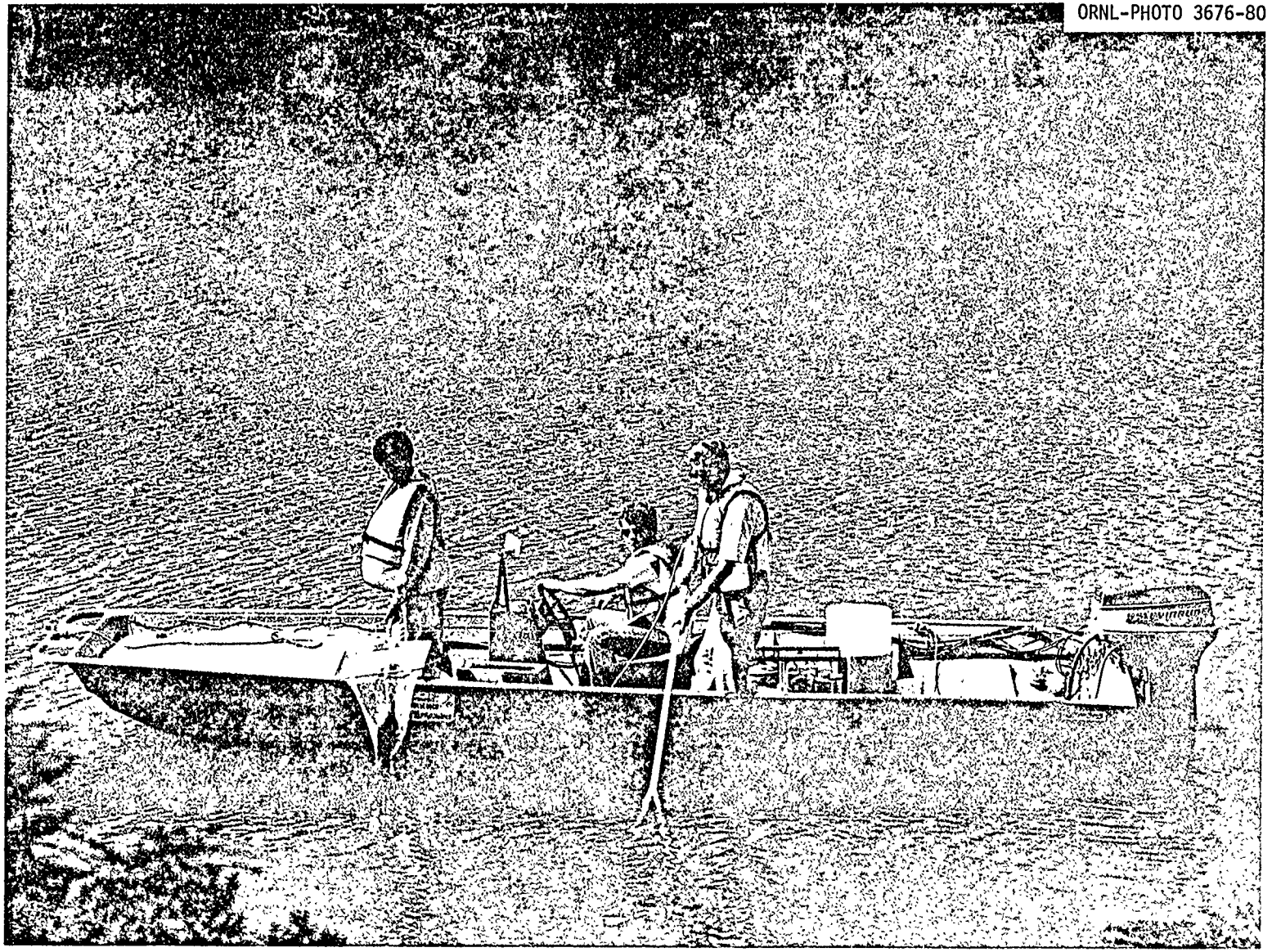

Fig. 3.2-1. An electric probe is inserted in the water to collect fish samples.

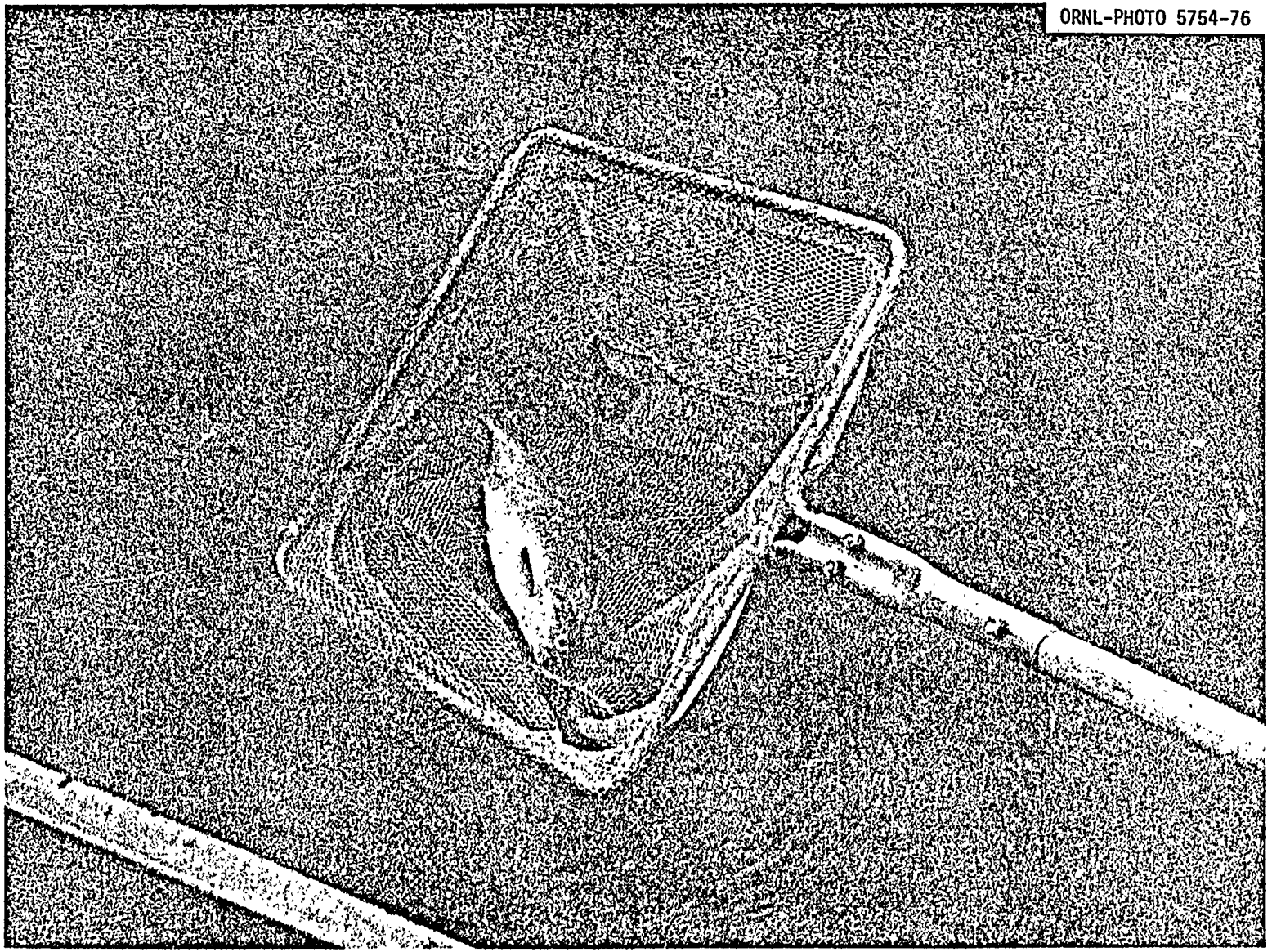

Fig. 3.2-2. Fish are captured in a net.

Fig. 3.2-3. Commercial food products.

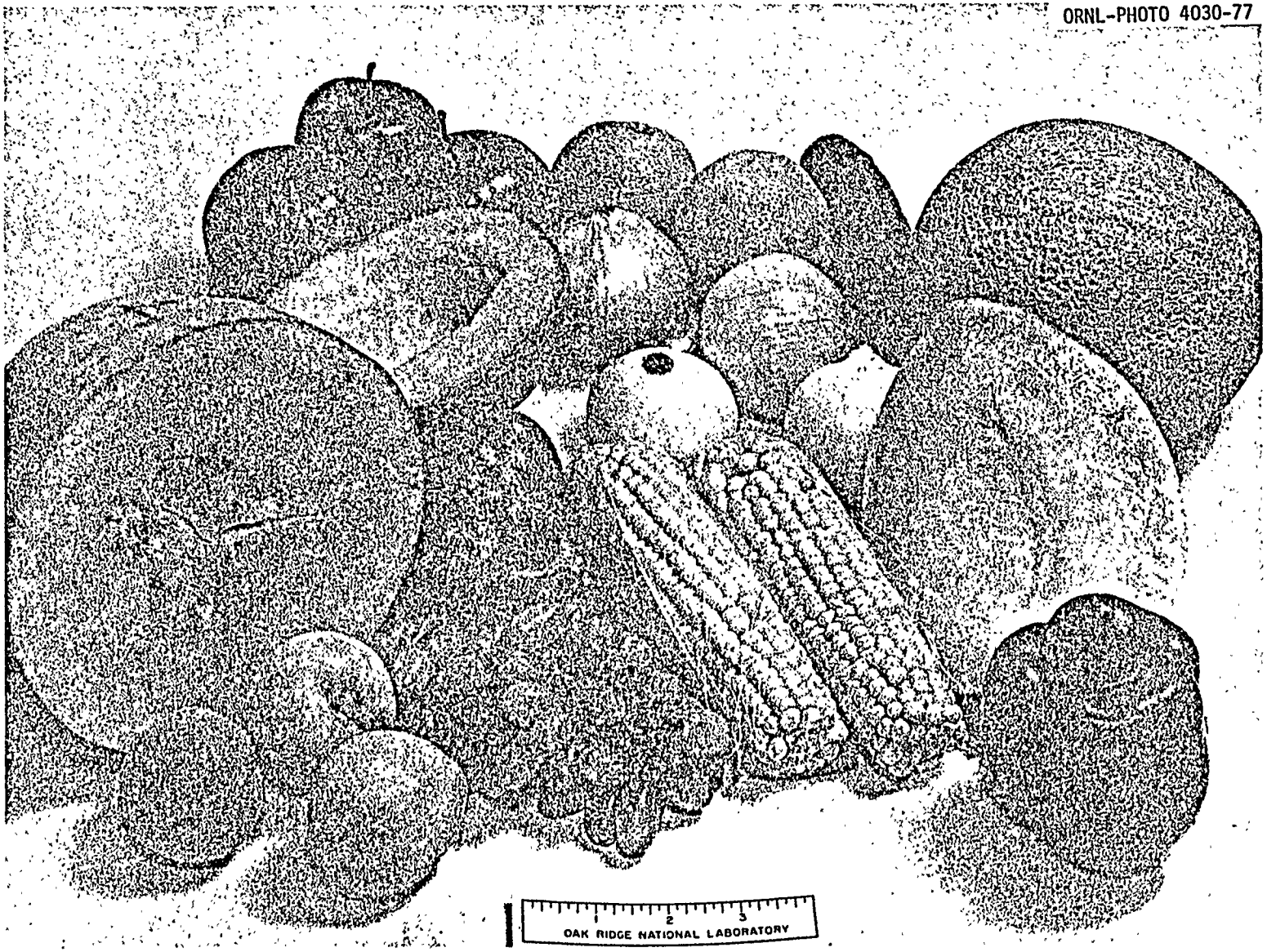

Fig. 3.2-4. Local food products.

The food samples (frozen or thawed) are prepared according to the water content of the sample. Samples with high water content are prepared using a Waring blender. Samples with low water content are chopped manually. The weight of the beaker, the weight of the beaker and food, and the actual weight of the food product are recorded. The beaker is labeled and covered with a quartz glass.

4. The following procedures are used to dry-ash biological samples.
   - 4.1 Place beakers containing samples in a muffle furnace (Fig. 3.2-5) at 100°C and leave overnight.
   - 4.2 Raise temperature to 150°C for 5 h. WATCH CAREFULLY TO PREVENT OVERFLOW.
   - 4.3 Raise temperature to 180°C for 5 h, then to 220°C for 5 h. Leave samples overnight in the furnace at 220°C.
   - 4.4 Punch holes in the ashing samples with a stirring rod.
   - 4.5 Raise temperature to 250°C for 3 or 4 h, to 280°C for 3 or 4 h, and to 300°C for overnight.
   - 4.6 Punch holes in the ashing samples and raise temperature to 325°C for 2 h, then to 350°C for 2 to 3 h. The samples may be left overnight in the furnace if necessary.
   - 4.7 Raise temperature by 20°C at 2- to 3-h intervals and leave overnight between 400 and 425°C.
   - 4.8 Raise temperature to 450°C until the samples are ashed (Fig. 3.2-6).

Note: Ashing procedures vary for different types of biological samples (e.g., fish, vegetables, and other food products). In general, the greater the water content, the slower the ashing process should be performed.

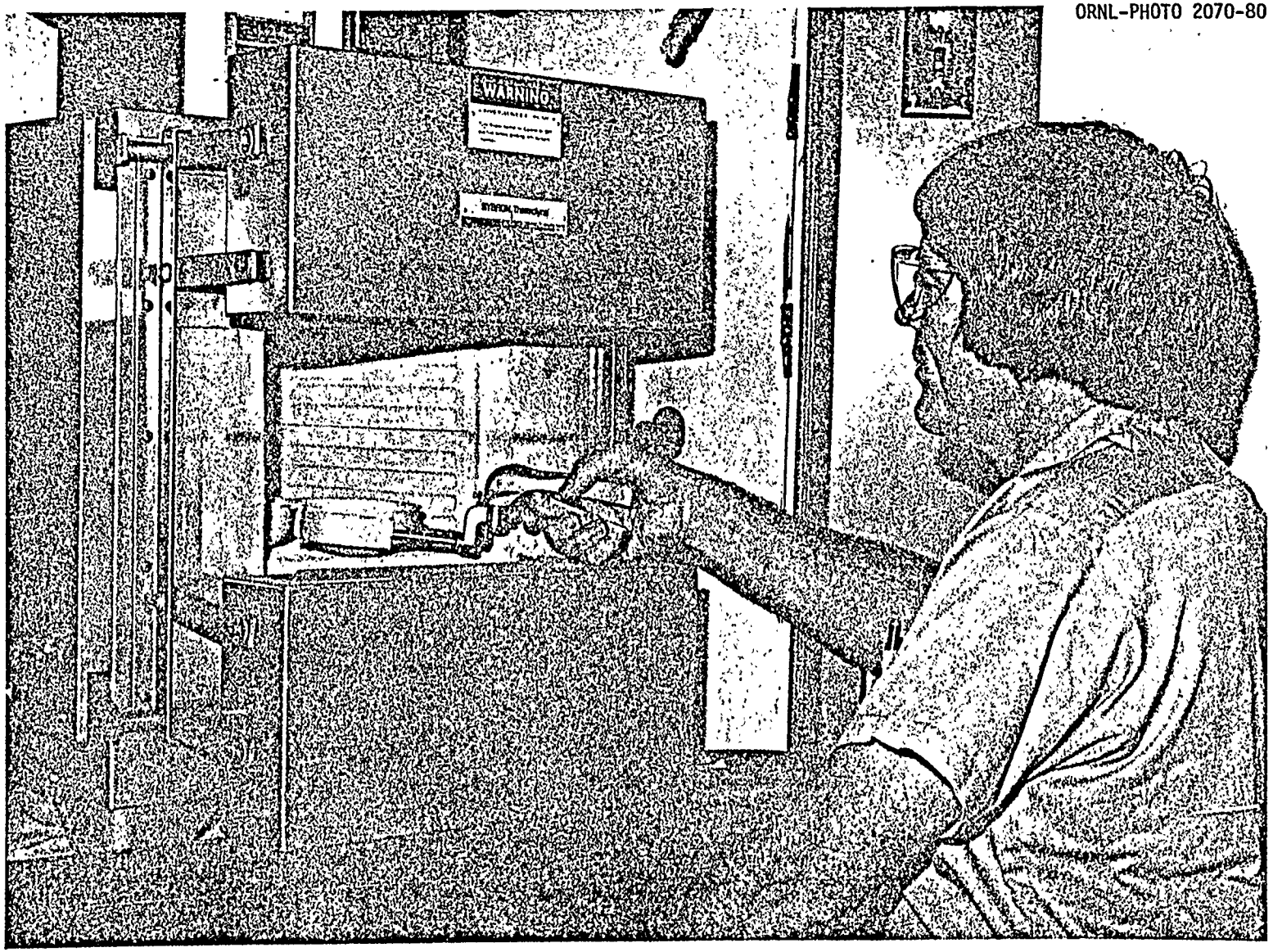

Fig. 3.2-5. Samples are placed in a muffle furnace.

ORNL-PHOTO 5701-76

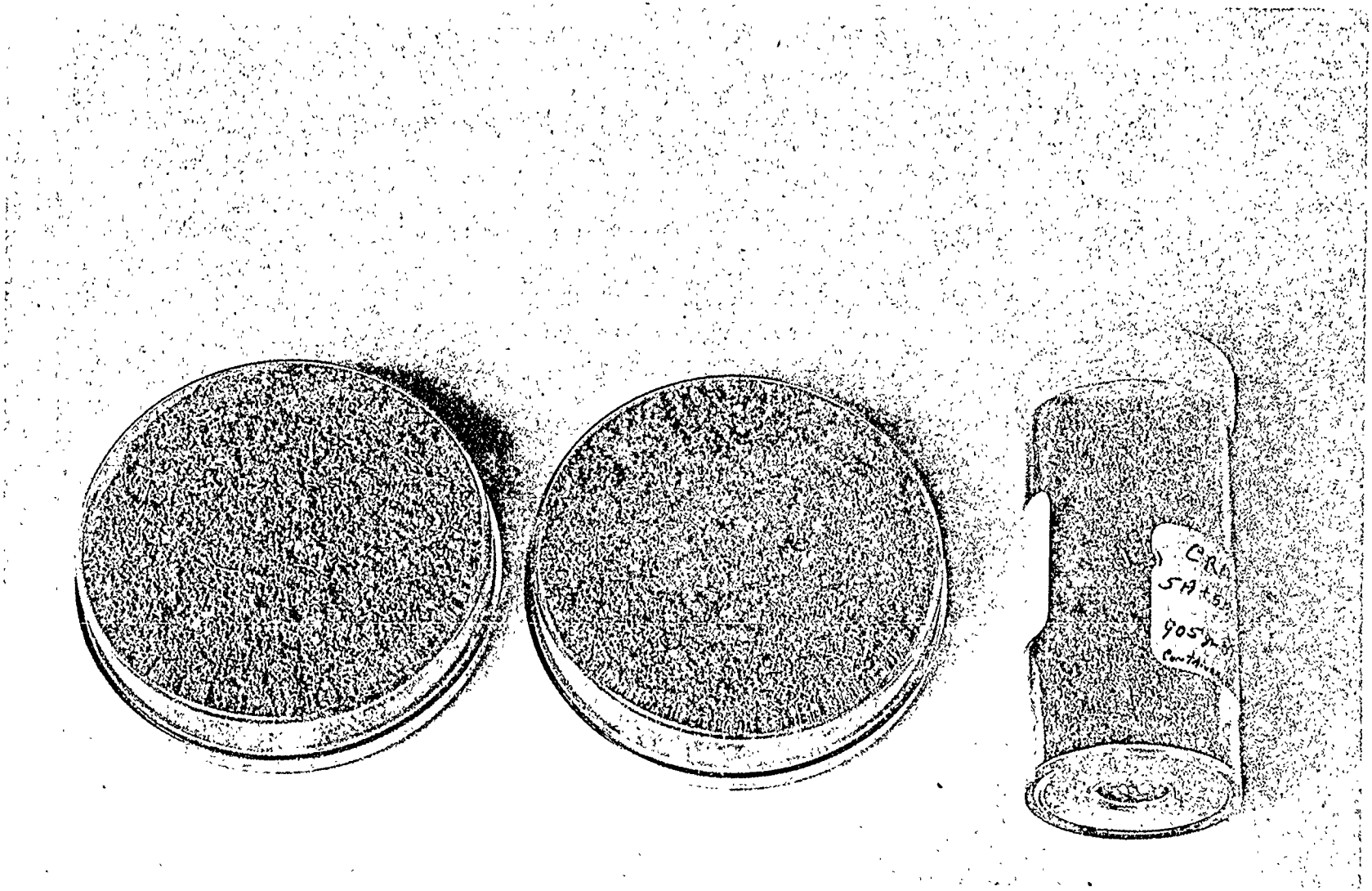

Fig. 3.2-6. Ash of fish samples after exposure to 450°C in muffle furnace.

3.3 Prepration of Ducks for Analysis

Ducks on White Oak Lake (WOL) are caught in a Sullivan trap (180 x 65 x 65 cm) using corn as bait. The traps are checked three times daily. If a duck has been captured, it is removed with care and placed in a cardboard box. The box provides enough darkness to decrease the excitement of the duck. The duck is brought to the laboratory.

In the laboratory, the duck is removed from the box and placed in a cotton sleeve (stocking) leaving the head free. The duck is placed on the table with its feet pulled toward the tail. The stocking is taped to secure the feet, and the bill is marked with a number, using a black waterproof pen. The duck is placed in a plastic box (30 x 30 x 30 cm) and counted for gamma emitters.

The gamma spectrometric analysis is similar to that presented in Sects. 2.3 and 2.4. The ducks are counted for 10 to 15 min and are released in the general area of capture.

3.4 Prepration of Bees for Gamma Spectrometric Analysis

The Department of Environmental Management has placed six bee hives in the Oak Ridge area; three bee hives are located on the banks of White Oak Lake (WOL), two on Chestnut Road, and one in the area of Burial Ground No. 6. The bee hives (Fig. 3.4-1) consist of brood chambers and supers. The brood chamber is located at the base of the hive and has ten racks. The bees grow on the pollen stored in the brood chamber. The supers have nine racks; each rack has a sheet of foundation which serves as a start for the bees. The racks in the brood chamber and super are 22.8 x 47.5 cm.

The bee hives are checked weekly from March to July and twice a month from August to December for an adequate supply of honey (needed for the bees' survival during the winter). The technician is advised to wear a bee helmet with a veil, white overalls taped at the sleeves and legs, and leather gloves (Fig. 3.4-1). It is further advised that a bee smoker, filled with burlap or pine needles, be ablaze while checking the bee hives.

In March and April the bee hives are examined for an adequate supply of pollen, production of honey, and eggs. In April, five of the brood chamber racks should be filled with eggs and five of the super racks should be filled with honey (6.8-9.1 kg). If the egg production is low, the queen bee should be replaced.

Later, when the bees have made a surplus of honey, the super racks can be exchanged with unused racks. The racks are returned to the laboratory where the cone/honey is cut from the racks. The honey is strained through a doubled cheese cloth into a beaker labeled with the date and location of collection. The cone is placed in a container labeled with the same information. The honey and cone are delivered to the Analytical Chemistry Counting Facility for gamma spectrometric analysis.

Bees (1000 drones and 1000 workers) are captured with a net made of cheese cloth. The bees are placed in double plastic bags, labeled with the date and location of collection, and taken to the laboratory. A brood rack containing the young bees and pollen is also taken to the laboratory.

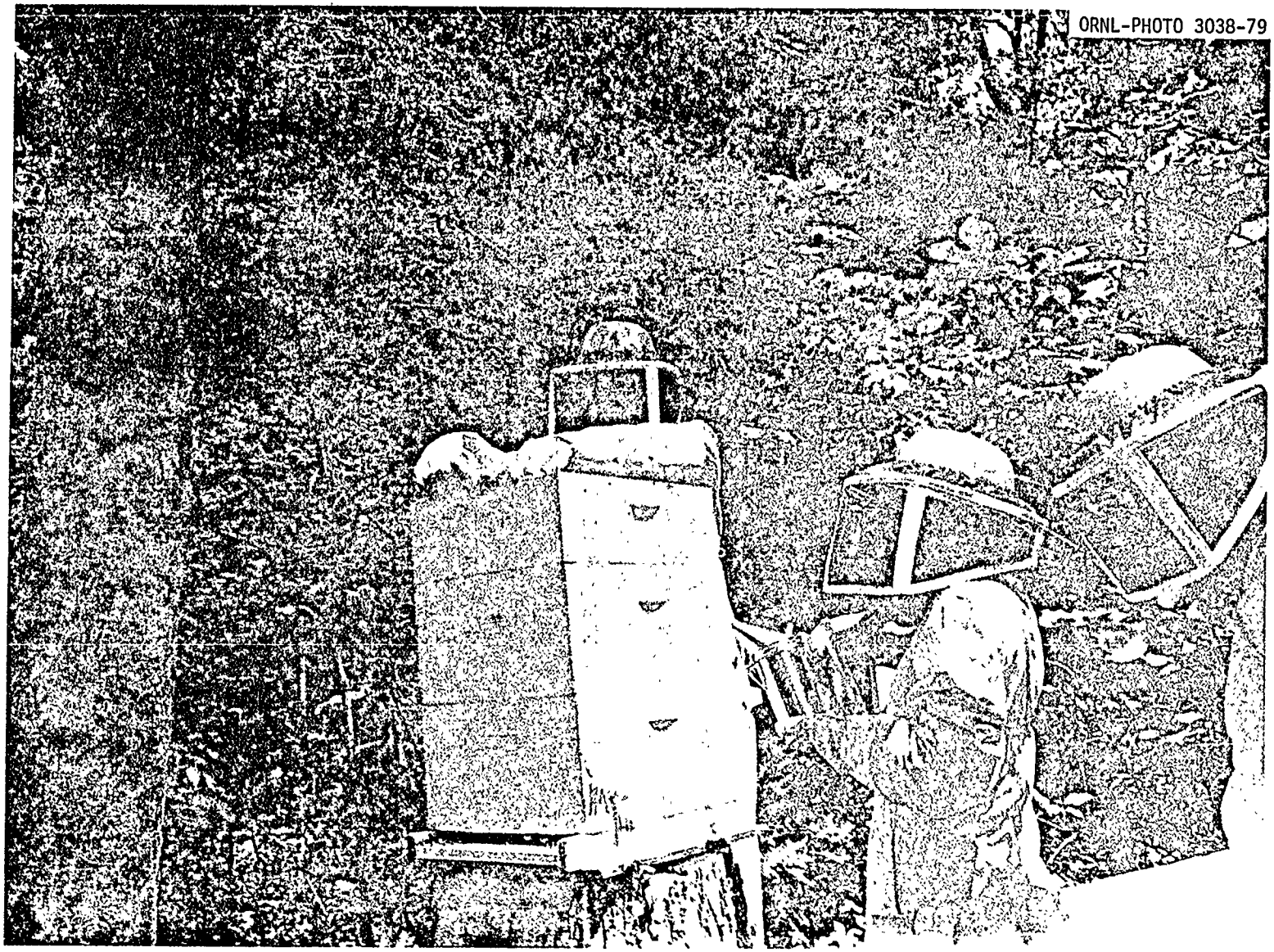

Fig. 3.4-1. Beehives are checked weekly.

At the laboratory, the bees are frozen. One hundred grams of pollen, taken from the brood chamber, is placed in a polyethylene vial labeled with the date and location of collection. The bees and pollen are delivered to the Analytical Chemistry Counting Facilities for gamma spectrometric analysis.

The gamma spectrometric analyses are similar to those presented in Sects. 2.3 and 2.4.

3.5 Preparation of Insects for Analysis

Insect traps are located in the general areas of LAMs 2, 4, 6 and 12, White Oak Dam and Shale Fracture areas. Each trap consists of an ultraviolet lamp (which attracts the insects) and several traps on which the insects are sorted according to size (Fig. 3.5-1). The insects are collected from the traps two to three times weekly and placed in a plastic bag labeled with the site location and the date of collection. The samples are returned to the laboratory and frozen.

Weekly, the insects are composited (according to the station) in a 1-L Marinelli beaker or 20 to 30 g petri dish. The sample containers are labeled with the site location and the week of collection. The samples are delivered to the Analytical Chemistry Counting Facility for gamma spectrometric analysis. For details on the gamma spectrometric analysis, refer to Sects. 2.3 and 2.4.

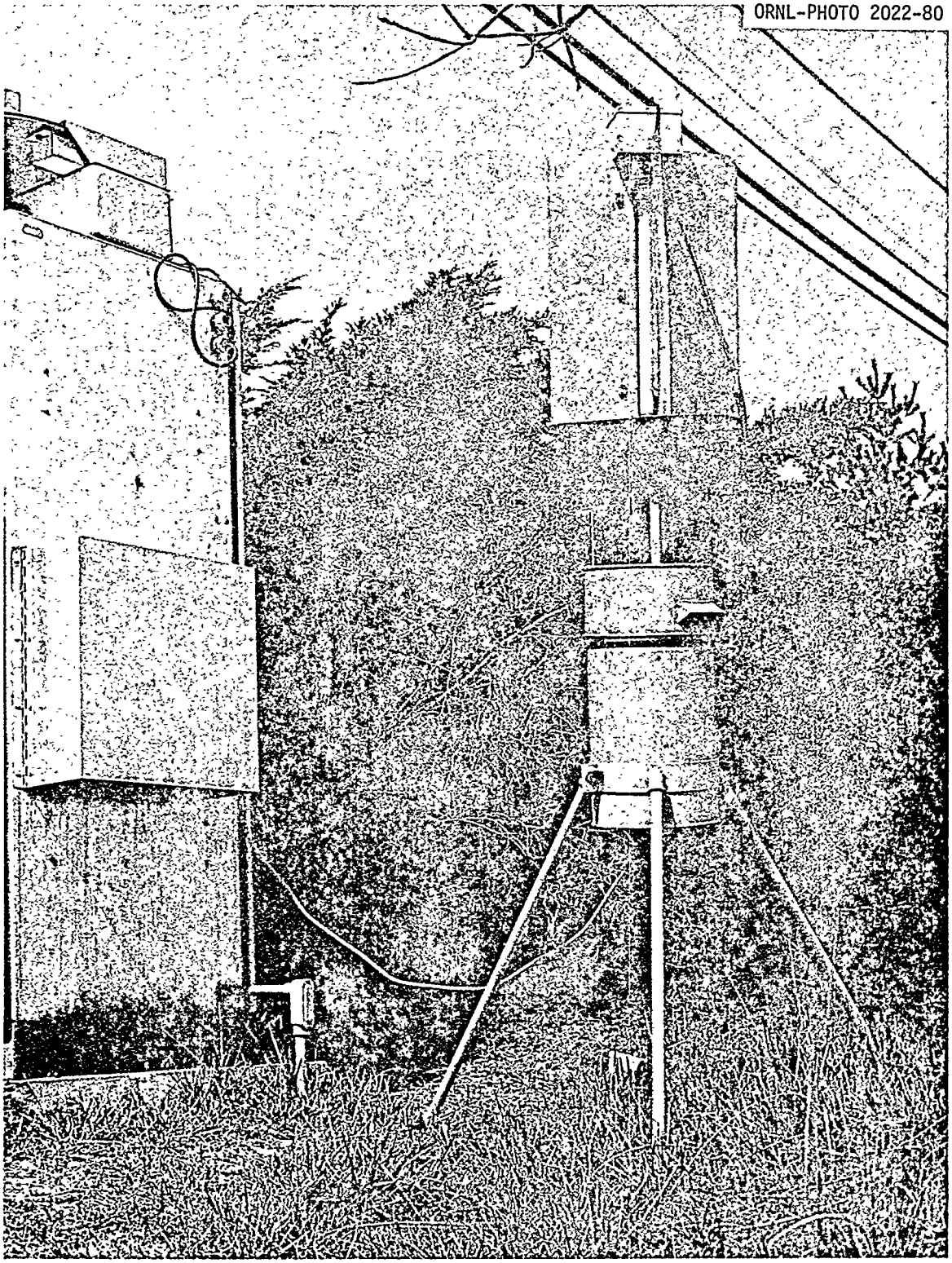

Fig. 3.5-1. An insect trap.

3.6 A General Discussion of Radionuclides Identification in Biological Samples Using the Whole Body Counter and Gamma Spectrometric Analysis

The Whole Body Counter (WBC) is located in a specially designed, low background room with walls 30-cm thick; these walls are constructed of concrete with additional layers of iron (8.9 mm), lead (3 mm), tin/cadmium (1 mm), and copper (0.2 mm). In addition to the specially designed walls, an air system continuously ventilates the counting room. The air system is composed of "aged" air which has been stored long enough for the natural working-level values of radon-222 and its progeny to be minimal. The WBC is primarily used by the Department of Environmental Management "scan" road-killed deer (Fig. 3.6-1). The deer are double bagged before they are taken to the WBC for analysis (see Sect. 3.1). Individual samples of deer tissue are mixed, blended, and put into a beaker for analysis, see Sect. 2.4.

The WBC contains two types of detectors. The first type consists of two NaI(Tl) crystals and detects pulse-height energies greater than 1 keV. A 23 x 23 cm crystal is located below the counting platform bed. Even though the crystals are primarily used for lung counts, they may also be used for whole-body scanning. The output of the pulse-height analyzer (256 channels) is fed into a ND-6620 computer and analyzed by programs developed specifically for this data processing system.

The library of standards is comprised of various fission product radionuclides which have been injected into an animal phantom made of polyethylene (approximately tissue-equivalent) and counted by the WBC. A gamma spectrum for each radionuclide injected and an uncontaminated animal spectrum are stored in the library of standards.

The second type of detector system consists of two phoswich detectors which detect energies below 100 keV. Many of these photons arise from x-ray emissions in the antinide series. Each phoswich detector has a 1.5-mm layer of NaI(Tl) and a 50-mm layer of CsI(Tl). If an interaction takes place in both the NaI(Tl) and CsI(Tl) crystals, a pulse-shape discrimination circuit prevents the pulse from entering the pulse-analyzer. This effect usually occurs from Compton scattering, pair

Fig. 3.6-1. Road-killed deer being scanned.

production, and/or background radiation. In cases where the total energy is absorbed only in the NaI(Tl) crystal (low-energy photons primarily interacting by the photoelectric process), the response is registered in the pulse-height analyzer.

3.7 Routing Procedures for the Collection of Milk Samples

In most cases, milk samples are collected within a few hours after the cows have been milked. Except for Broadacres Dairy, no pasteurization or sterilization has been performed on the milk samples. It is desirable that the cream be separated from the milk samples before collection; if not, it is removed from samples and discarded before analysis.

Before leaving ORNL, one must obtain $19.50 ($3.50 in quarters and $16 in single bills) or $22, if performing the Knoxville/Norris run from the ORNL Cashier and have the receipt forms. Each milk producer is required to sign a receipt stating the amount of money that he or she has been paid for the milk sample.

In addition to the weekly local samples, remote samples are collected for background information. Each remote station is visited once every 5 weeks. The routing procedures for the remote milk stations are also presented.

3.7.1 Routing Procedures for Weekly Local Milk Sampling Stations

Information presented here includes the optimum route for travel to designated milk stations, individuals involved in the transactions, quantity of milk collected, fee paid, and other pertinent information. Usually 2 liters of milk is collected at each station and the individual is paid $2.50 for the sample ($2.00 for Broadacres sample).

Figure 3.7-1 shows the locations of the local milk sampling stations. Milk samples are collected each Wednesday from stations in the following order for the most efficient operation.

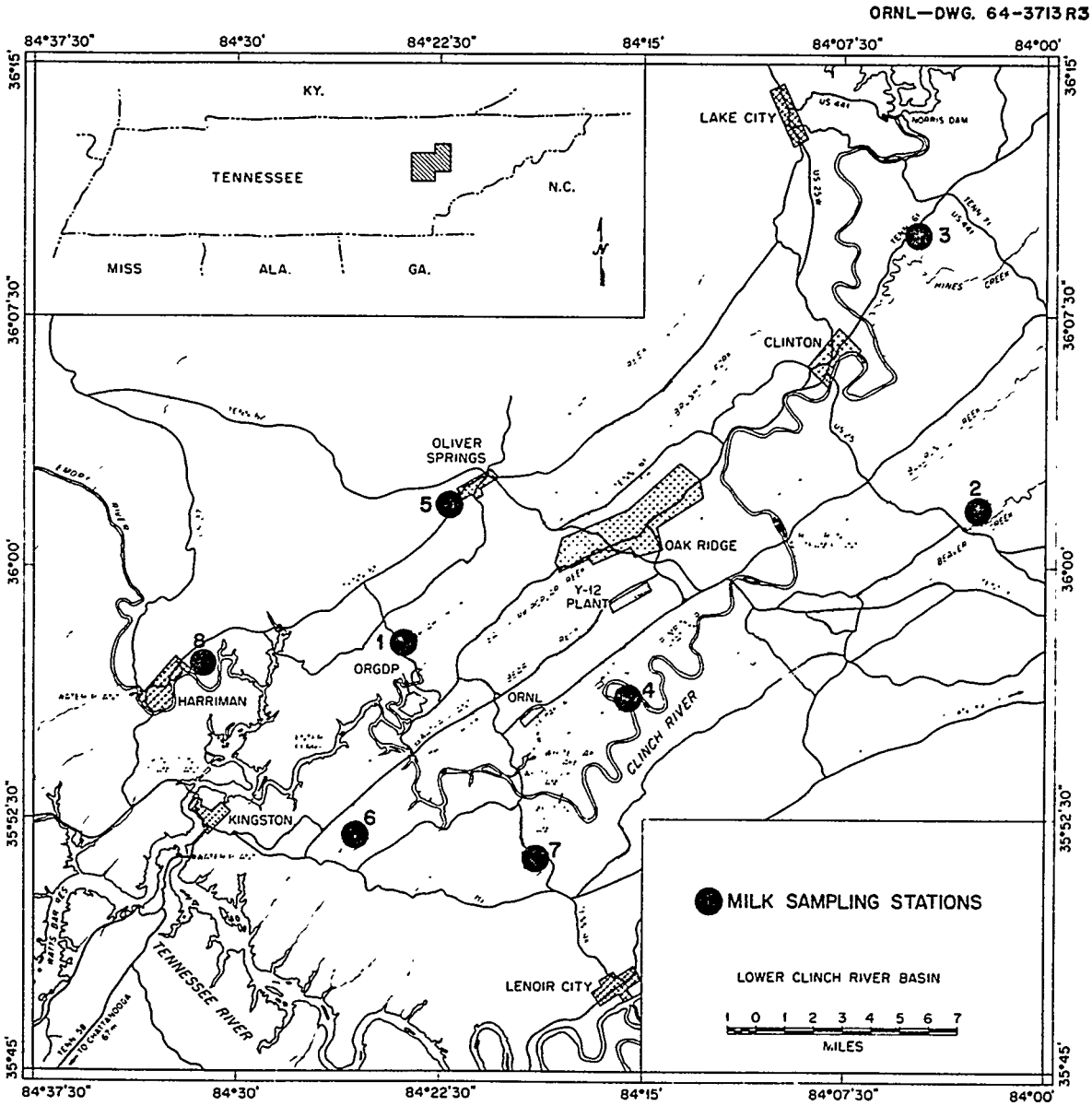

Fig. 3.7-1. Location of local milk sampling stations.

1. Comparative Animal Research Laboratory (CARL)* No. 3

Proceed east on White Oak Avenue.. Turn left onto Melton Valley Access Road and right onto Bethel Valley Road. Proceed east for approximately 9.7 km (6 miles). CARL is at the intersection of Bethel Valley Road and Carbide Park Access Road.

2. Broadacres (Weigels) – Mr. Hill and Mr. Head No. 2

Proceed approximately 0.8 km (0.5 mile) and exit onto Edgemoor Road. Proceed approximately 11 km (6.8 miles) and turn right onto Clinton Highway toward Powell. Turn left at the first red light onto Emory Road. Drive approximately 0.3 km (0.2 mile) and turn left onto Broadacres driveway. The Broadacres Dairy can be seen from the drive.

3. Clinton – Mrs. Miller No. 3

From Broadacres, turn right onto Emory Road and right onto Clinton Highway. Proceed approximately 6.6 km (4.1 miles). Turn right on Raccoon Valley Road (at Claxton Elementary School). Travel approximately 10.4 km (6.5 miles). Turn left onto Fleenor Mill Road (on left just prior to crossing interstate). Proceed approximately 2.3 km (1.4 miles). Turn right onto Wolf Valley Road. Travel approximately 0.3 km (0.2 mile) and turn left prior to overpass of intersection. Do not go under interstate. Go approximately 1.8 km (1.1 miles) and turn left at a red barn. Travel approximately

*The CARL milk station is the same as the Clinton station. If the milk is not at CARL, proceed to Broadacres after collecting the sample; from the Broadacres station proceed to Oliver Springs by way of Clinton Highway (25W). Approximately 7 km (4.4 miles) from Broadacres, turn right onto Highway 61W. Proceed approximately 9 km (5.6 miles) through Clinton and turn right onto Highway 61W toward Oliver Springs. Travel about 11.4 km (7.1 miles), turn right onto a four-lane highway and go about 4.3 km (2.7 miles). Turn right onto Spring Street at the red light in Oliver Springs. Proceed for about 2.4 km (1.5 miles) on Spring Street and cross over a bridge. Turn left onto Frost-Bottom Road and travel about 3.5 km (2.2 miles). A T-intersection sign can be seen in front of the house. The milk station is to the right.

1.6 km (1 mile) and turn right onto Look Out Tower Road. Turn right at Y-intersection and continue for approximately 1.1 km (0.7 mile). The milk can be collected from the house at the end of the road.

4. Oliver Springs (Frost Bottom) — Mrs. Lively No. 4

From Mrs. Miller, return to the intersection of Look Out Tower Road and Wolf Valley Road. Turn right toward Clinton and proceed approximately 4.7 km (2.9 miles) to a T-intersection. Turn left at the T-intersection and travel approximately 0.16 km (0.1 mile) to new Highway 61. Travel approximately 2.6 km (1.6 miles). Turn right onto Highway 61 and proceed approximately 9 km (5.6 miles) through Clinton. Turn right onto Highway 61W toward Oliver Springs. Travel approximately 11.4 km (7.1 miles), turn right onto a four-lane highway and proceed approximately 4.3 km (2.7 miles). Turn right onto Spring Street at the red light in Oliver Springs. Proceed approximately 2.4 km (1.5 miles) on Spring Street and cross over a bridge. Turn left onto Frost Bottom Road and travel approximately 3.5 km (2.2 miles). The milk station is on the right. A T-intersection sign can be seen in front of the house.

5. Harriman — Mrs. Lyle No. 6

Return to Oliver Springs. Turn right onto Tri-County Boulevard (Highway 61W) and to the immediate left after crossing railroad tracks. Proceed on Highway 61W toward Harriman for approximately 17.9 km (11.1 miles) until Highway 61W runs into Highway 27S. Travel approximately 3.9 km (2.4 miles) and turn left by Wood Chapel Methodist Church's sign. Turn to the immediate left. The milk can be collected at the house on the left (a dark wooden house surrounded by farm equipment).

6. Blair — Hatmaker No. 1

Return to the main highway. Turn right onto Highway 61E/27N toward Oliver Springs. Travel approximately 11.9 km (7.4 miles) until an Exxon station is seen on the left. Turn at the first right

onto Blair Road. Proceed for approximately 4.3 km (2.7 miles). Turn left onto Poplar Creek Road. Cross the bridge and turn left at the first driveway. The milk can be collected from Mr. Hatmaker at the white brick house on top of the hill. Go to the door in the carport.

7. Bradbury — Hensley No. 7

Return to Blair Road and turn left. Proceed for approximately 4.8 km (3 miles). Turn right onto Highway 58S. Travel approximately 10.5 km (6.5 miles). Turn left at the T-intersection onto Highway 70. Travel approximately 2.4 km (1.5 miles) and turn left at the I-40 sign onto Bradbury Community Road. Travel approximately 1.3 km (0.8 mile). The milk can be collected at the crab orchard (tan) house on the right. Hensley is written on the mailbox.

8. Hardin Valley — Long No. 5

Continue on Bradbury Community Road/Buttermilk Road for approximately 6.3 km (3.9 miles) to I-40. Proceed toward Knoxville on I-40. After the merging of I-40 and I-75, proceed for approximately 0.8 km (0.5 mile) and exit at Watt Road. Turn left onto Watt Road and to the immediate right onto Everett Road. Travel approximately 1.6 km (1 mile). Turn left onto Yarnell Road. After approximately 1.2 km (0.75 mile), a barn resembling a hotel can be seen on the right. The milk can be collected at the white house on the left.

9. To return to ORNL

Return to I-40 (west-bound). Travel approximately 6.3 km (3.9 miles), exit at Melton Hill/Highway 95 and turn right on Highway 95. Proceed approximately 2 miles and turn right onto Lagoon Road. Enter ORNL at the west end.

3.7.2 Individual Routing Procedures for Weekly Local Milk Sampling Stations

In emergencies or unusual situations when a milk sample must be collected from an individual sampling station (rather than from the

entire route), the following procedures for reaching the milk sampling stations from ORNL should be used.

1. Blair — Mr. Hatmaker No. 1

   Proceed east on White Oak Avenue through the East Vehicle Gate. Go through the parking lot and turn left onto Bethel Valley Road. Proceed for approximately 1.6 km (1 mile). Turn right onto Highway 95 and left onto Highway 58. Turn right onto Blair Road. Cross over a single-lane bridge. Turn right onto Poplar Creek Road. Cross the bridge and turn left at the first driveway. Mr. Hatmaker lives in the first house on the right (white brick). Go to the door in the garage.

2. Broadacres (Weigels) — Mr. Hill and Mr. Head No. 2

   Proceed east on White Oak Avenue. Turn left onto Melton Valley Access Road and right onto Bethel Valley Road. Proceed for approximately 11.3 km (7 miles) and turn right onto Edgemoor Road. Turn right onto Clinton Highway and left onto Emory Road. Turn left by entrance sign to Broadacres. Broadacres milk station is approximately 28.3 km (17.6 miles) from ORNL.

3. Comparative Animal Research Laboratory (CARL) — Mr. Miller No. 3

   Proceed east on White Oak Avenue. Turn left onto Melton Valley Access Road and right onto Bethel Valley Road. Proceed east for approximately 9.7 km (6 miles). CARL is at the intersection of Bethel Valley Road and Carbide Park Access Road.

4. Oliver Springs (Frost Bottom) — Ms. Lively No. 4

   Proceed east on White Oak Avenue. Turn left onto Melton Valley Access Road and right onto Bethel Valley Road. Proceed for approximately 9.7 km (6 miles). Turn left onto Scarboro Road at the Y-intersection. Continue on Scarboro Road to Illinois Avenue. Cross over the Oak Ridge Turnpike (Highway 95) and travel to downtown Oliver Springs. Turn right onto Spring Street, cross over

the bridge, and turn left onto Frost Bottom Road. Proceed approximately 3.6 km (2.2 miles). The milk station is on the right. A T-intersection sign can be seen in front of the house.

5. Hardin Valley — Long No. 5

Proceed on White Oak Avenue through the East Vehicle Gate. Drive through parking lot and turn left onto Bethel Valley Road. Proceed for approximately 1.6 km (1 mile). Turn left onto Highway 95 and proceed approximately 4.8 km (3 miles). Turn left onto I-40. Merge left at I-40/75 intersection toward Knoxville. Proceed approximately 0.8 km (0.5 mile) and exit on Watt Road. Turn left onto Watt Road and right immediately after crossing over the interstate onto Everett Road. Travel for approximately 1.6 km (1 mile). Turn left onto Yarnell Road and travel approximately 1.2 km (0.75 mile). A barn resembling a hotel can be seen on the right; the house is on the left.

6. Harriman — Mrs. Lyles No. 6

Proceed east on White Oak Avenue through East Vehicle Gate. Turn left and drive through parking lot. Turn left onto Bethel Valley Road and proceed for approximately 3.2 km (2 miles). Turn left onto Highway 95 and proceed for approximately 4.8 km (3 miles). Turn right onto I-40 and proceed to Harriman. Exit at Harriman/Rockwood and turn right toward Harriman. Continue through Harriman to the north side of town. Turn right at the Wood Chapel Church sign. Collect milk at the first dark wooden house (converted house trailer) on left surrounded by farm equipment.

7. Bradbury — Mr. Hensley No. 7

Proceed on White Oak Avenue through East Vehicle Gate and turn left. Drive through parking lot and turn left onto Bethel Valley Road. Proceed for approximately 3.2 km (2 miles). Turn left and proceed on Highway 95 and drive for approximately 4.8 km (3 miles). Turn right onto I-40. Exit on Buttermilk Road. Turn right and proceed

approximately 6.4 km (4 miles). Look for Hensley's name on the mailbox. The house is made of crab orchard stone (tan). A white garage is at the end of the driveway.

3.7.3 Routing Procedures for Remote Milk Sampling Stations

Collections are made from the remote milk sampling stations on a 5-week schedule. Figure 3.7-2 shows the locations of these stations. They may be reached by the following procedures.

1. Stinking Creek — Mrs. Broyles — (Norris) No. 51

   Proceed east on White Oak Avenue and turn left onto Melton Valley Access Road. Turn right and proceed east on Bethel Valley Road. Turn right onto Edgemoor Road. Continue across Clinton Highway (Highway 25W) onto Raccoon Valley Road. Turn left onto I-40 and continue to Stinking Creek exit. Exit and turn right onto Stinking Creek Road. Travel approximately 4 km (2.5 miles) or until a white house can be seen on the right. Mr. Charles Broyles No. 3 is written on the mailbox. If no one is at home, the milk will be on the porch or in the stream in front of the house. The receipt will be with the milk or in the mailbox.

2. Philadelphia Milk Station (Watts Bar) No. 52

   Proceed on White Oak Avenue through East Vehicle Gate. Turn left and drive through the parking lot. Turn left onto Bethel Valley Road and proceed approximately 1.6 km (1 mile). Turn left onto Highway 95 to I-75. Turn right onto I-75, exit at Philadelphia, and turn right. Turn to the immediate right onto a gravel road. The milk sample can be collected at the end of the road. The milk station is approximately 64.4 km (40 miles) from ORNL.

3. Sevierville Milk Station — Mr. Hodge No. 53

   Proceed east on White Oak Avenue. Turn left onto Melton Valley Access Road. Turn right onto Bethel Valley Road and drive for approximately 10.5 km (6.5 miles). Cross over Solway Bridge and continue to Knoxville on Highway 162 (Pellissippi Parkway). Merge

ORNL DWG 76-12775RA

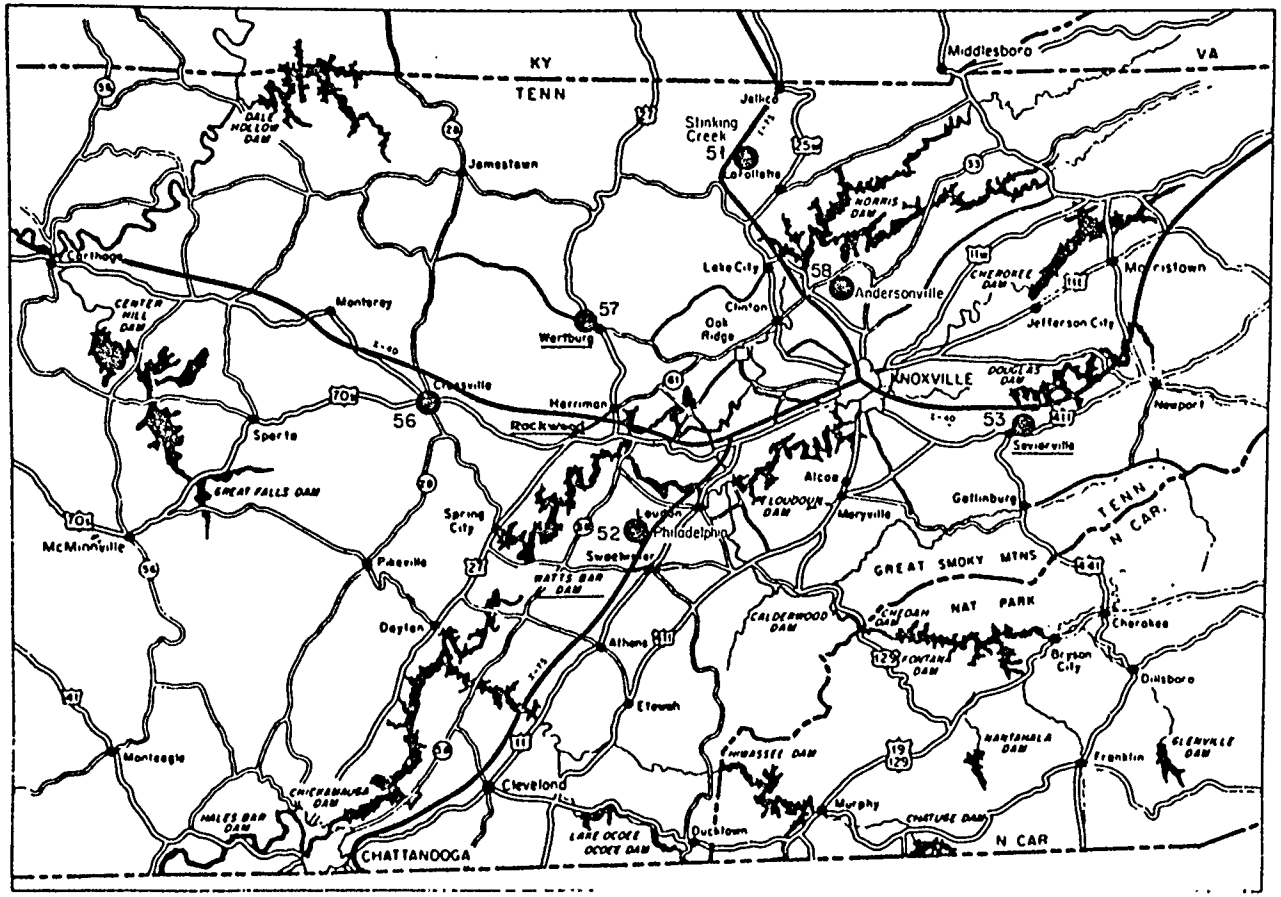

Fig. 3.7-2. Location of remote milk sampling stations.

left onto I-40/75. Continue through Knoxville on I-40. Exit at 406/Sevierville. Turn right toward Sevierville on Highway 66. Highway 66 is a two-lane highway. Just before Highway 66 becomes a four-lane highway, turn left onto Douglas Dam Road (dead-end road). Continue on this road until a large barn with Catlett Brothers' Farm written on it can be seen. Collect the milk at the small concrete building on the right. The milk station is approximately 105 km (65 miles) from ORNL.

4. Crossville Milk Station — No. 56

Proceed on White Oak Avenue to the east parking lot. Drive through the parking lot and turn left onto Bethel Valley Road. Continue on Bethel Valley Road to the intersection of Highway 95 and turn right. Proceed approximately 1.4 miles and turn left onto Bear Creek Road. Continue on Bear Creek Road, passing under Highway 58 and turn right onto the second road (∿4.1 miles). Turn right onto Highway 58 and proceed to Kingston. Approximately 4.1 miles, turn right onto I-40 W. Travel approximately 38.8 miles to exit 317, the Crossville/ Jamestown exit. Turn left and travel toward Crossville on Highway 127/28 S. Turn right onto Highway 70 W at the first traffic light. Proceed to the intersection of Highway 70 S and 70 W and turn right (corner of K-mart) onto Highway 70 S. Proceed approximately 8 miles and turn left onto driveway. A sign indicating the availability of Hereford cows is across from the driveway and a pond is near the driveway. The house is white and surrounded by a pasture with a barn. When conducting the routing, the individual should back track to ORNL or return to the intersection of Highway 70 S and Highway 70 W and proceed to Great Falls and Dale Hollow.

5. Wartburg — Heidels' (Dale Hollow) No. 57

Proceed east on White Oak Avenue and turn left onto Melton Valley Access Road. Turn right onto Bethel Valley Road. Proceed approximately 9.7 km (6 miles) and turn left at the Y-intersection onto Scarboro Road. Continue on Scarboro Road to Illinois Avenue and cross over Oak Ridge Turnpike. Continue on Illinois Avenue

(Highway 62) to Oliver Springs [approximately 8 km (5 miles)]. Turn right onto Highway 61 in Oliver Springs. At the T-intersection (Wartburg) turn right and drive into Wartburg. At the Shell service station in Wartburg, turn left. Go by the church, turn left, and drive approximately 1.1 km (0.7 mile). The Heidels' home will be on the right. The Heidels' large mailbox is painted silver.

6. Andersonville — Bobby George No. 58

Proceed east on White Oak Avenue and turn left onto Melton Valley Access Road. Turn right and proceed east on Bethel Valley Road. Turn right onto Edgemoor Road. Continue across Clinton Highway (Highway 25W) onto Raccoon Valley Road. Turn left onto I-40 and continue to Clinton/Norris (Highway 61) exit. Turn right onto Old Highway 61 toward Norris. Go through Andersonville to the north side of town. A large white mailbox is at the driveway. The milk barn is at the end of the driveway, past the house.

3.8 Analysis for Radioiodine in Milk

(Performed by Bio-Assay Laboratory, Industrial Safety and Applied Health Physics)

1. Reagents

   1.1 Iodine carrier, 10 mg/ml with a few mg of sodium bisulfite ($NAHSO_3$)

   1.2 Dowex-1, X-8, 20-50 mesh

   1.3 Sodium chloride (NaCl) 2M

   1.4 Nitric acid (HNO_3) concentrated

   1.5 Hydroxylamine hydrochloride ($NH_2OH \cdot HCl$)

   1.6 Sodium bisulfite ($NaHSO_3$) 1M (freshly prepared)

   1.7 Silver nitrate ($AgNO_3$) (10 mg Ag^+ per ml)

   1.8 Sodium hypochlorite (NaOCl), 4-6%

   1.9 Carbon tetrachloride (CCl_4)

2. Apparatus

   2.1 Ion exchange columns

   2.2 Magnetic stirrer

   2.3 Vacuum flask, 500-ml

   2.4 Separatory funnels, 250-ml

3. Procedure

   3.1 Prepare a resin column, 1.5 cm in diameter, using 20 ml of wet resin (1-X8, 20-50 mesh in distilled water) and attach it in series with a cation exchanger for strontium-90 sorption. Refer to "Analysis for Radiostrontium in Milk" (Sect. 3.9).

   3.2 Add 1 ml of iodine carrier to approximately 2 liters of the fresh milk sample. (The cream is removed first by aspiration; therefore, the sample will be less than 2 liters in most cases.)

   3.3 Pass the milk sample over the columns at a flow rate of approximately 10 ml/min.

   3.4 Wash the columns with 2 liters of hot tap water.

   3.5 Separate the strontium column and wash the iodine column with an additional 1 liter of hot tap water. Refer to "Analysis of

Radiostrontium in Milk" (Sect. 3.9) for further preparation of the strontium column.

3.6 Wash the iodine column with 100 ml of 2M NaCl solution and discard the wash. The column must be neutral or basic.

3.7 Transfer the resin plus slurry from the column to a 250-ml beaker using NaOCl. Add 2 ml of 1M NaOH.

3.8 Heat to near boiling on a hot plate.

3.9 Stir for 5 min with a 1-in. magnetic stirring bar.

3.10 Assemble a filter funnel with a 500-ml vacuum flask and filter the solution into the flask using suction. Whatman No. 40 filter paper should be used.

3.11 Pour solution with resin into the funnel. Wash resin from beaker with 25 ml of NaOCl and 25 ml of distilled water. Pour this solution into the funnel. After filtration, discard the resin.

3.12 In the hooded area, add 20 ml of concd HNO_3 and boil 5 to 10 min on a hot plate. Cool.

3.13 Transfer the solution to a 250-ml separatory funnel. Use approximately 25 ml of distilled water to rinse sample from beaker. Add solution to separatory funnel.

3.14 Add approximately 1.5 g of $NH_2OH \cdot HCl$ and 50 ml of CCl_4 to sample.

3.15 Extract for 2 min (shaking constantly) or until the CCl_4 phase of the sample becomes purple.

3.16 Drain the CCl_4 into a clean 250-ml beaker.

3.17 Add approximately 1.0 g of $NH_2OH \cdot HCl$ to the sample in the separatory funnel and reextract with 40 ml of CCl_4 (shaking constantly).

3.18 Drain the CCl_4 extraction into the beaker containing the first CCl_4 extraction. Discard the aqueous solution.

3.19 Add 25 ml of distilled water and 1 ml of 1M $NaHSO_3$ solution to the CCl_4 solution of iodine.

3.20 Extract the solution for 2 min (shaking constantly) and allow to settle for 10 min. The solution should be colorless.

3.21 Separate the organic (cloudy portion) from the aqueous portion by draining the solution into two beakers.

3.22 Repeat Steps 3.19 and 3.20 using the cloudy portion (CCl_4) of the sample.

3.23 Separate the organic and aqueous phases. The aqueous portion can be drained into the beaker with the first aqueous extraction. Discard the organic portion.

3.24 Add 2 ml of concd HNO_3 to the solution with a 1-in. magnetic stirring bar.

3.25 While stirring, add 5 ml of $AgNO_3$ solution.

3.26 Remove the stirring bar and digest the solution on a hot plate until the silver iodide (AgI) coagulates (a yellowish white coagulate).

3.27 Transfer the solution plus precipitate to a centrifuge tube. Rinse sample from tube with distilled water. Centrifuge for 5 min.

3.28 Discard supernate and add 10 ml of acetone to the residue.

3.29 Filter the sample through a Whatman No. 40 filter disk using suction.

3.30 Place filter on a counting disk and allow to sit overnight.

3.31 Place the disk in the gas-flow GM counter and count for 60 min. A 20-min background count and a 10-min reference count (using a strontium-90 source) should also be obtained.

3.32 An 80% yield factor should be applied in determining the concentration of radioiodine in the milk sample. This yield factor has been predetermined through statistical analysis from previous standard milk samples.

NOTE: The percentage yield for iodine extracted from each milk sample cannot be determined directly because of the iodized salt already present in the milk.

3.33 Apply appropriate self-absorption and decay factors to determine an accurate concentration of radioiodine (iodine-131) in each milk sample.

Working Bibliography for Sect. 3.8

Health and Safety Laboratory, U.S. Atomic Energy Commission, *Procedure Manual*, HASL-300.

3.9 Analysis for Radiostrontium in Milk

(Performed by Bio-Assay Laboratory, Industrial Safety and Applied Health Physics)

1. Reagents

   1.1 Hydrochloric acid (HCl) 6M

   1.2 Nitric acid (HNO_3) 6M, concd

   1.3 Hydrogen peroxide (H_2O_2) 30%

   1.4 Fe^{+3} carrier solution (3 mg/ml)

   1.5 Ammonium hydroxide (NH_4OH) concd

   1.6 Dowex 50W-X8, 50-100 mesh cation exchange resin (hydrogen form).

2. Special Equipment

   2.1 Ion exchange columns

   2.2 Platinum wire stirrer

   2.3 Stainless steel planchets

   2.4 Low-level beta GM counter.

3. Procedure

   3.1 Prepare a resin column, 1.5 cm in diameter, using 20 ml of wet resin (50W-X8, 50-100 mesh in distilled water) and attach it in series with a cation exchanger for iodine-131 absorption. Refer to "Analysis for Radioiodine in Milk" (Sect. 3.8).

   3.2 Remove the surface cream from the milk sample by aspiration. Add 1 ml of the iodine carrier to approximately 2 liters of the milk sample (Sect. 3.8).

   3.3 Pass the milk sample over the columns at a flow rate of approximately 10 ml/min.

   3.4 Wash the columns with 2 liters of hot tap water. This wash is performed to remove the butterfat from the column.

   3.5 Separate the iodine column from the strontium column. Wash the strontium column with an additional 2 liters of hot tap water. Refer to "Analysis of Radioiodine in Milk" (Sect. 3.8), for further preparation of the iodine column.

3.6 Wash the strontium column with 500 ml of 0.5M HCl and then with 200 ml of distilled water. Discard these washings. These washings are done to remove any alkali metals which are loosely bound to the column.

3.7 Add 200 ml of 6M HNO_3 and collect in a beaker. Allow to sit for two weeks so that yttrium-90 buildup can reach secular equilibrium with its parent, strontium-90.

3.8 After two weeks, evaporate the solution to dryness.

3.9 Ash the sample two or three times with concd HNO_3 and 30% H_2O_2. The ashing is done to remove any organic contaminant from the elutriant. The peroxide is added to supply oxygen for the HNO_3 reaction to consume any organic material.

3.10 Dissolve the final residue in 15 to 20 ml of distilled water and 1 drop to 1 ml of concentrated HCl (2M). Transfer this solution to a centrifuge tube. Rinse the beaker with a minimum volume of distilled water and add to the centrifuge tube.

3.11 Add 0.5 ml (1.5 mg) of the Fe^{+3} solution [$Fe(OH)_3$]. Iron(III) hydroxide is used as a carrier for the precipitation reaction. Add 3 ml of concd NH_4OH to the centrifuge tube. This will increase the pH of the solution to about 8.0. [$Fe(OH)_3$ will precipitate at about pH 4.0.]

3.12 Stir the solution with a platinum wire to initiate the precipitation reaction.

3.13 Centrifuge and discard the supernate.

3.14 Wash the precipitate with about 10 ml of distilled water and centrifuge. Discard this wash. Redissolve in dilute acid (1 ml HCl/20 ml H_2O) and reprecipitate with NH_4OH. Then wash with about 10 ml of distilled H_2O and 1 drop NH_4OH and centrifuge again.

3.15 Transfer precipitate to a stainless steel planchet with 6M HNO_3 (0.5 to 1.0 ml). The transfer can be done by using a pipette.

3.16 Dry the sample under a heat lamp before counting.

3.17 Place the planchet in the gas-flow GM counter and count for 100 min. A 20-min background count and a 10-min reference count (using a strontium-90 source) should also be obtained.

3.18 To determine the concentration of radiostrontium in the milk sample, an 80% yield factor should be applied. The yield factor has been predetermined through statistical analysis of previous standard milk samples.

3.19 Apply appropriate self-absorption due to heavy precipitation, counting efficiency, and decay factors to determine accurately the concentration of radiostrontium (strontium-90) in each milk sample.

4. Calculations

4.1 Reagent background (Bkgd) = 0

4.2 Efficiency of counter = 80%

4.3 Background of counter = 0.5 counts/min

4.4 Efficiency factor = 3.2 dis/count (reciprocal of percent efficiency)

4.5 Equilibration time = 7 days (168 h)

4.6 Total counts/min:

4.6.1 Determining counts/min of yttrium-90 (sister to strontium-90 with half-life of 64 h):

Assume 5 counts/min - 0.5 counts/min (Bkgd) = 4.5 counts/min

4.6.2 Efficiency factor:

4.5 counts/min x 3.2 dis/count = 14.40 dis/min

4.6.3 Counting efficiency:

$$\frac{14.40}{0.8} = 18.0 \text{ dis/min of yttrium-90}$$

4.6.4 Formula for calculating activity of strontium-90 in sample:

$$N_2 = \frac{N_1\lambda_1}{\lambda_2 - \lambda_1}(e^{-\lambda_1 t} - e^{-\lambda_2 t})$$

As $\lambda_1 \to 0$, $e^{\lambda_1 t} \to 1$

$$N_2 = \frac{N_1\lambda_1}{\lambda_2 - \cancel{\lambda_1 0}}(\cancel{e^{-\lambda_1 t 0}} - e^{-\lambda_2 t})$$

$$N_2 = \frac{N_1\lambda_1}{\lambda_2}(1 - e^{-\lambda_2 t})$$

$$\lambda_2 N_2 = N_1 \lambda_1 (1 - e^{-\lambda_2 t})$$

$$A_2 = A_1 (1 - e^{-\lambda_2 t})$$

$$A_1 = \frac{A_2}{(1 - e^{-\lambda_2 t})}$$

where

N_1 = number of atoms of ^{90}Sr,
N_2 = number of atoms of ^{90}Y,
λ_1 = decay constant for ^{90}Sr (2.89×10^{-6}/h),
λ_2 = decay constant for ^{90}Y (0.011/h),
t = time required for separation of ^{90}Sr from ^{90}Y (in hours),
$A_1 = \lambda_1 N_1$ = activity of ^{90}Sr,
$A_2 = \lambda_2 N_2$ = activity of ^{90}Y.

4.6.5 Correct dis/min of ^{90}Y for decay from beginning of analysis to end, that is, if the analysis takes 4 h, then:

$$A = A_0 e^{\lambda t}$$

$$A_0 = A e^{\lambda t}$$

A_0 = 18 dis/min and $e^{\lambda t} = 1.045$, thus A_0 = 18.8 dis/min.

Then assuming separation requires one week:

$$A_1 = \frac{A_2}{(1-e^{-\lambda_2 t})}$$

$$A_1 = \frac{18.81}{[1-e^{-.011(168)}]}$$

$$A_1 = \frac{18.81}{1-0.16} = 22.33 \text{ dis/min.}$$

3.10 Radiochemical Method for Determining Plutonium in Fish (performed by Analytical Chemistry Division Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

   1.1 This method is applicable to the determination of the isotopes of plutonium in fish samples.

2. Summary of Method

   2.1 The dissolved sample is equilibrated with plutonium-242, which is used as an internal standard; subsequently, plutonium is reduced to Pu^{+3} and carried on calcium fluoride. After dissolution, plutonium is oxidized to Pu^{+4}, adsorbed on anion exchange resin, reduced to Pu^{+3}, and selectively eluted from the resin. Plutonium in the effluent solution is carried on praseodymium hydroxide, dissolved, and oxidized to Pu^{+4}, which is then extracted with thenoyltrifluoroacetone-xylene. The organic extract is evaporated on a stainless steel disk that is analyzed by alpha pulse-height analysis to determine the concentrations of plutonium isotopes.

   2.2 The lowest reported concentration is 7.4×10^{-4} Bq/g (2×10^{-2} pCi/g) of ashed sample.

3. Sample Handling and Preservation

   3.1 Fish samples are weighed to determine the wet weight, dried in an oven at 105°C, and ashed in a muffle furnace at 525°C until free of carbon. The ashed weights are measured, and the ratios of wet weight to ashed weight are determined.

   3.2 Ashed samples are stored in airtight glass or plastic containers.

4. Interferences

   4.1 Calcium and phosphate are major chemical interferences.

   4.2 Alpha pulse-height analysis eliminates alpha interferences except for plutonium-240, which cannot be resolved from plutonium-239 by pulse-height analysis.

5. Apparatus

5.1 Drying oven

5.2 Muffle furnace

5.3 Hot plate

5.4 Centrifuge

5.5 Vortex mixer

5.6 Extraction vials, 50-ml with plastic-lined screw caps

5.7 Lab glassware

5.7.1 Beakers, 150-ml size and 500-ml tall-form

5.7.2 Centrifuge tubes, 50-ml glass and 100-ml plastic

5.7.3 Glass ion exchange column, 8-mm-ID by 25-cm-long, fitted with a stopcock

5.8 Transfer pipettes

5.9 Stainless steel disks

5.10 Multichannel analyzer system with silicon surface-barrier detector(s).

6. Reagents

6.1 Hydrochloric acid (HCl), 0.1M: Add 8.3 ml of concd HCl to 500 ml of water and dilute to 1 liter with water.

6.2 Nitric acid (HNO_3), 8M: Add 500 ml of concd HNO_3 to 500 ml of water.

6.3 Nitric acid (HNO_3), concentrated

6.4 Nitric acid-aluminum nitrate solution: Dissolve 250 g of aluminum nitrate nonahydrate [$Al(NO_3)_3 \cdot 9H_2O$] in 500 ml of 8M HNO_3.

6.5 Ammonium hydroxide (NH_4OH), concentrated

6.6 Plutonium-242 tracer: Dilute an NBS-certified (or equivalent) solution of plutonium-242 to a concentration of 10 dis min^{-1} ml^{-1} with 2M HNO_3 and store in glass.

6.7 Nitric acid (HNO_3), 2M: Add 125 ml of concd HNO_3 to 500 ml of water and dilute to 1 liter with water.

6.8 Nitric acid (HNO_3), 1M: Add 500 ml of 2M HNO_3 to 500 ml of water.

6.9 Sodium bisulfite ($NaHSO_3$), powder

6.10 Sodium nitrite ($NaNO_2$), crystals

6.11 Sodium fluoride (NaF) solution, saturated: Add 45 g of NaF to 1 liter of water and mix thoroughly.

6.12 Thenoyltrifluoroacetone (TTA)-xylene solution, 0.5M TTA: Dissolve 111 g of $SC_4H_3COCH_2COCF_3$ (TTA) in xylene and dilute to 1 liter with xylene.

6.13 Ferric nitrate solution, 0.1M: Dissolve 40.4 g of ferric nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$] in water and dilute to 1 liter with water.

6.14 Hydroxylamine hydrochloride solution, 5M: Dissolve 347.5 g of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in water and dilute to 1 liter with water.

6.15 Hydrochloric acid-hydroxylamine hydrochloride solution, 0.5M HCl-0.05M $NH_2OH \cdot HCl$: Add 42 ml of concd HCl and 10 ml of 5M $NH_2OH \cdot HCl$ to 500 ml of water and dilute to 1 liter with water.

6.16 Praseodymium carrier solution: Dissolve 12.82 g of praseodymium nitrate dihydrate [$Pr(NO_3)_3 \cdot 2H_2O$] in 500 ml of water and dilute to 1 liter with water.

6.17 Anion exchange resin: Dowex 1-X4 (50-100 mesh, chloride form) or equivalent.

6.18 Sodium hydroxide (NaOH) solution, 6M: Dissolve 240 g of NaOH in 500 ml of water and dilute to 1 liter with water.

6.19 Hydrochloric acid (HCl), 8M: Add 666 ml of concd HCl to 334 ml of water.

6.20 Sodium nitrite solution ($NaNO_2$), 3M: Dissolve 10.4 g of $NaNO_2$ in water and dilute to 50 ml with water. Make fresh daily.

7. Procedure

7.1 Transfer a known weight of ashed sample (5 to 10 g) to a 500-ml tall-form beaker, add enough 4M HCl to moisten, and take to dryness on a hot plate.

7.2 Add enough concd HNO_3 to wet the sample and take to dryness on a hot plate.

7.3 Repeat step 7.2 until the sample is the consistency of heavy syrup.

7.4 Dissolve the residue with heat in 0.1M HCl and dilute to 100 ml with 0.1M HCl.

7.5 Add 1 ml of plutonium-242 tracer solution of a precisely known disintegration rate.

7.6 Adjust the sample solution to a pH range of 1.0 to 1.5 using 6M NaOH.

7.7 Add approximately 0.1 g of $NaHSO_3$ per gram of ashed sample.

7.8 Place on hot plate and bring near to boiling while stirring.

7.9 Reduce heat and continue to digest for 2 h at 50°C while maintaining the volume with water. Plutonium reduces to Pu^{+3}.

7.10 Remove the sample from the hot plate and slowly stir in saturated NaF until the sample solution begins to cloud.

7.11 Stir frequently for the next 30 min. Allow the precipitate to settle overnight.

7.12 Decant the supernatant solution, transfer the precipitate to a 100-ml plastic centrifuge tube, centrifuge for 10 min at 2000 rpm, and discard the supernatant solution.

7.13 Wash the precipitate with water, centrifuge for 10 min. at 2000 rpm, and discard the wash solution.

7.14 Dissolve the precipitate in 5 to 10 ml of HNO_3-$Al(NO_3)_3$ solution. Transfer the dissolved sample to a 150-ml beaker using 8M HNO_3 to rinse the centrifuge tube.

7.15 Adjust the volume to 50 ml with 8M HNO_3, add 250 mg of $NaNO_2$ crystals, place on hot plate, rapidly bring to a boil, and immediately remove from heat.

7.16 Allow the sample to digest for 20 min in the oxidizing solution to oxidize plutonium to Pu^{+4}.

7.17 While the sample is digesting, prepare a resin column as follows.

7.17.1 Place a glass-wool plug in the bottom of the column described in step 5.7.3.

7.17.2 Slurry the resin (see step 6.17) with water and immediately discard the fines by decanting. Repeat as necessary until fines are removed.

7.17.3 Transfer 4 ml of the resin to the column with water. Prevent any channeling by maintaining the solution level above the resin using the stopcock.

7.17.4 Place a glass-wool plug on top of the resin.

7.17.5 Convert the resin to the nitrate form by passing several column volumes of 8M HNO_3 through the column until the resin is free of chloride ions.

7.18 Transfer the sample solution, which should be at room temperature, to the prepared resin column and allow it to flow through the column at a rate of 2 ml/min. Discard the effluent solution.

7.19 Rinse the beaker with 25 ml of 8M HNO_3 and transfer the rinse to the column. Allow the 8M HNO_3 rinse to flow through the column at a rate of 2 ml/min. Discard the effluent solution.

7.20 Rinse the beaker with 25 ml of 8M HCl and transfer the rinse to the column. Allow the 8M HCl rinse to flow through the column at a rate of 2 ml/min. Discard the effluent solution.

7.21 Add one drop of 0.1M $Fe(NO_3)_3$ and 1 ml of 5M $NH_2OH \cdot HCl$ to the column. Open the stopcock and allow the solution to drain to the top of the resin bed, then stop the flow. Discard the effluent solution.

7.22 Add 4 ml of 0.5M HCl-0.05M $NH_2OH \cdot HCl$ solution. Place a 50-ml glass centrifuge tube under the column. Allow 3 ml of solution to drain into the tube and close the stopcock.

7.23 Allow 20 min digestion time for reduction of the plutonium to Pu^{+3}.

7.24 Add 25 ml of 0.5M HCl-0.05M $NH_2OH \cdot HCl$ solution. Pass the solution through the column at a flow rate of 2 ml/min into the 50-ml tube.

7.25 Add 1 ml of praseodymium carrier to the sample solution in the 50-ml tube and mix thoroughly.

7.26 Add concd NH_4OH with stirring to a pH of 9. Allow 15 min digestion time.

7.27 Centrifuge for 10 min at 1500 rpm and discard the supernatant solution.

7.28 Wash the precipitate with water, centrifuge, and discard the water-wash solution.

7.29 Dissolve the precipitate in six drops of concd HNO_3 and transfer the dissolved sample to a 50-ml extraction vial with 5 ml of 1M HNO_3. Add 10 drops of 3M $NaNO_2$, mix well, and allow 20 min digestion time.

7.30 Add 1 ml of 0.5M TTA-xylene solution and extract on a Vortex mixer for 10 min.

7.31 Centrifuge for 2 min to separate the phases. Discard the aqueous phase.

7.32 Scrub the TTA extract with 5 ml of 1M HNO_3. Centrifuge and discard the aqueous phase.

7.33 Transfer the TTA to a stainless steel disk placed on a hot plate set at 150°C. Allow the TTA to dry thoroughly.

7.34 Flame the stainless steel disk to a red heat.

7.35 Measure the alpha activities by pulsing with a silicon surface-barrier detector coupled to a multichannel analyzer.

8. Calculations

$$^{238}Pu = ACM/DE \text{ , Bq/g ,}$$
$$^{239}Pu = BCM/DE \text{ , Bq/g ,}$$

where

A = net integrated counts of ^{238}Pu from pulse analysis,
B = net integrated counts of ^{239}Pu from pulse analysis,
C = dis/min of ^{242}Pu added,
D = net integrated counts of ^{242}Pu from pulse analysis,
E = weight of sample,
M = conversion factor to Bq; 1 Bq = 60 dis/min.

9. Precision and accuracy

9.1 The precision is estimated to be ±20%. The accuracy has not been established.

Working Bibliography for Sect. 3.10

George H. Coleman, *The Radiochemistry of Plutonium*, National Academy of Sciences — National Research Council, NAS-NS 3058 (Sept. 1, 1965).

John H. Harley (ed.), *HASL Procedures Manual*, HASL-300 (current).

Frederick B. Johns (ed.), *Handbook of Radiochemical Analytical Methods*, EPA-680/4-75-001 (February 1975).

3.11 Radiochemical Method for Determining Strontium-90 in Fish (performed by Analytical Chemistry Division Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

   1.1 This method is applicable to the determination of strontium-90 in fish.

2. Summary of Method

   2.1 Strontium-90 is determined indirectly by measuring the yttrium-90 daughter activity ($T_{1/2}$ = 64 h).

   2.2 Yttrium carrier is equilibrated with the dissolved sample, precipitated as the fluoride and hydroxide, extracted into tributyl phosphate (TBP), back-extracted from the organic phase, precipitated as the hydroxide, and finally precipitated as the oxalate, which is mounted for beta counting and counted on a low-background beta counter.

   2.3 The lowest reported concentration is 0.74×10^{-3} Bq/g (2×10^{-2} pCi/g) of ashed sample.

3. Sample handling and preservation

   3.1 Fish samples are weighed to determine the wet weight, dried in an oven at 105°C, and ashed in a muffle furnace at 525°C until free of carbon. The ashed weights are measured, and the wet weight to ashed weight ratios are determined.

   3.2 Ashed samples are stored in airtight glass or plastic containers.

4. Interferences

   4.1 Calcium and phosphate are major chemical interferences.

   4.2 High concentrations of rare earth beta emitters interfere in the beta counting of yttrium-90. Decay counting is recommended for a purity check.

5. Apparatus

   5.1 Drying oven

   5.2 Muffle furnace

5.3 Hot plate

5.4 Centrifuge

5.5 Vortex mixer

5.6 Filter flask and funnel

5.7 Low-background beta counter

5.8 Extractions vials, 50-ml with plastic-lined screw caps

5.9 Lab glassware

5.9.1 Beakers, 50-ml size and 500-ml tall-form

5.9.2 Centrifuge tubes, 50-ml glass and 100-ml plastic

5.10 Filter paper, Whatman No. 541 (11 cm), Whatman No. 1 (18 mm).

5.11 Transfer pipettes

5.12 Analytical balance

5.13 Fritted-glass filter crucibles

5.14 Desiccator

6. Reagents

6.1 Hydrochloric acid (HCl), 0.1M: Add 8.3 ml of concd HCl to 500 ml of water and dilute to 1 liter with water.

6.2 Hydrochloric acid (HCl), 4M: Add 333 ml of concd HCl to 500 ml of water and dilute to 1 liter with water.

6.3 Hydrochloric acid (HCl), 6M: Add 500 ml of concd HCl to 500 ml of water.

6.4 Hydrochloric acid (HCl), concentrated

6.5 Nitric acid (HNO_3), 8M: Add 500 ml of concd HNO_3 to 500 ml of water.

6.6 Boric acid (H_3BO_3) solution, saturated: Add 55 g of H_3BO_3 to 1 liter of water and mix thoroughly.

6.7 Nitric acid (HNO_3), concentrated

6.8 Ammonium hydroxide (NH_4OH), concentrated

6.9 Sodium fluoride (NaF) solution, saturated: Add 45 g of NaF to 1 liter of water and mix thoroughly.

6.10 Oxalic acid solution, saturated: Add 110 g of $H_2C_2O_4 \cdot 2H_2O$ to 1 liter of water and mix thoroughly.

6.11 Tributyl phosphate (TBP), 100%

6.11.1 Equilibrate equal volumes of concd HNO_3 and 100% TBP by shaking for 2 min in a separatory funnel. Allow

phases to separate and discard the aqueous phase. Store the prepared TBP in glass.

6.12 Ethyl alcohol (C_2H_5OH), 95%

6.13 Diethyl ether ($C_2H_5OC_2H_5$), anhydrous

6.14 Yttrium carrier solution: Dissolve 18 g of yttrium nitrate hexahydate [$Y(NO_3)_3 \cdot 6H_2O$] in a minimum of HNO_3 and dilute to 1 liter with water.

6.14.1 Standardization of yttrium carrier: Pipette 5.00 ml of yttrium carrier solution into a 50-ml beaker, add 20 ml of water, heat the solution to boiling, and add 15 ml of a saturated oxalic acid solution with stirring. Transfer the precipitate (while it is still hot) to a previously tared filter crucible. Wash all of the precipitate from the beaker with hot water. Dry the precipitate using three 10-ml portions of 95% ethyl alcohol and two 10-ml portions of diethyl ether. Desiccate the crucible and precipitate to a constant weight. The net weight of the precipitate is the weight of yttrium oxalate, $Y_2(C_2O_4)_3 \cdot 9H_2O$, in 5.00 ml of the yttrium carrier solution.

7. Procedure

7.1 Transfer a known weight of ashed sample (5 to 10 g) to a 500-ml tall-form beaker, add enough 4M HCl to just moisten the sample, and take to dryness on a hot plate.

7.2 Add enough concd HNO_3 to thoroughly wet the sample and take to dryness.

7.3 Repeat step 7.2 until the sample is the consistency of heavy syrup.

7.4 Dissolve the residue in a minimum of 6M HCl with heat and dilute to 100 ml with 0.1M HCl.

7.5 Remove any undissolved material by filtering through Whatman No. 541 filter paper into another 500-ml beaker.

7.6 Add 2 ml of yttrium carrier solution to the sample.

7.7 Place the beaker containing the dissolved sample and carrier on a hot plate and heat to near boiling for 20 min to equilibrate.

7.8 Remove from the hot plate and slowly stir in saturated NaF until the sample begins to cloud.

7.9 Stir frequently for 30 min and allow the precipitate to settle overnight.

7.10 Decant the supernatant solution and transfer the precipitate to a 100-ml plastic centrifuge tube.

7.11 Centrifuge at 2000 rpm for 10 min and discard the supernatant solution.

7.12 Wash the precipitate with water, centrifuge at 200 rpm for 10 min, and discard the wash solution.

7.13 Dissolve the precipitate in a minimum of saturated H_3BO_3 and concd HNO_3.

7.14 Dilute with 15 ml of water and add concd NH_4OH to a pH of 9.

7.15 Centrifuge for 10 min at 2000 rpm and discard the supernatant solution. Wash the precipitate with water, centrifuge, and discard the wash solution.

7.16 Dissolve the precipitate in concd HNO_3.

7.17 Transfer the sample to a 50-ml extraction vial, rinsing the centrifuge tube with a minimum of concd HNO_3.

7.18 Add an equal volume of 100% TBP and extract for 10 min on a Vortex mixer.

7.19 Centrifuge for 2 min and discard the aqueous phase. Record time as separation time for yttrium-90.

7.20 Scrub the TBP with an equal volume of concd HNO_3, centrifuge, and discard the aqueous phase.

7.21 Add an equal volume of water to the TBP and backextract for 10 min on a Vortex mixer.

7.22 Centrifuge for 2 min.

7.23 Using a transfer pipette, transfer the aqueous phase to a 100-ml centrifuge tube.

7.24 Repeat steps 7.21, 7.22, and 7.23 two more times, combining the water strips in the same 100-ml centrifuge tube.

7.25 Discard the organic phase.

7.26 Add concd NH_4OH, with stirring, to a pH of 9.

7.27 Cool to room temperature, centrifuge, and discard the supernate.

7.28 Wash the precipitate with water, centrifuge, and discard the water wash.

7.29 Dissolve the precipitate with 2 ml of 6M HCl and dilute to 15 ml with water.

7.30 Heat to boiling and add 15 ml of saturated oxalic acid.

7.31 Place in an ice bath and stir to precipitate the yttrium oxalate.

7.32 Centrifuge and discard the supernate.

7.33 Place a tared 18-mm filter paper in the filtering funnel and wet with water, using vacuum on the filtering flask.

7.34 Transfer the precipitate onto the filter with hot water, wash with two 10-ml portions of hot water, three 5-ml portions of 95% ethyl alcohol, and two 5-ml portions of diethyl ether.

7.35 Weigh the filter paper and precipitate and determine the chemical recovery.

7.36 Mount the sample for beta counting and count on a low-background beta counter.

8. Calculations

$$^{90}Sr = ABM/DEF \ , \quad Bq/g \ ,$$

where

A = net counts per minute of purified ^{90}Y,

B = the efficiency factor for ^{90}Y,

D = fraction of yttrium carrier recovered,

E = fraction of ^{90}Y remaining at count time,

F = weight of ashed sample analyzed, and

M = conversion factor to Bq; 1 Bq = 60 dis/min.

9. Precision and Accuracy

9.1 The precision is estimated to be ±20%; no data are available for determining the accuracy.

Working Bibliography for Sect. 3.11

H. L. Krieger and S. Gold, *Procedures for Radiochemical Analysis of Nuclear Reactor Aqueous Solution*, EPA-R4-73-0114 (May 1973).

P. C. Stevenson and W. E. Nervik, *The Radiochemistry of the Rare Earths, Scandium, Yttrium, and Actinium*, National Academy of Sciences — Nuclear Science Series 3020 (February 1961).

4. WATER SAMPLING

The concentration of radionuclides in water is determined by the collection and analysis of rainwater and water samples from designated areas. These areas include Melton Hill Dam, White Oak Dam, White Oak Creek, K-25 water intake, Kingston water supply, and potable water at ORNL. Water samples are collected daily, weekly, or monthly depending on the location. The samples are analyzed by gamma spectrometry, ion exchange, atomic absorption, alpha range analysis, gravimetric, fluorometric, volumetric, colorimetric, turbidity, infrared, and other techniques.

4.1 Routing Procedures for Water Stations

1. Gallaher Water Sampling Station (GWSS)

Call K-25 Environmental Management Group (4-8223) before leaving ORNL. They will unlock the gate to the Gallaher Water Sampling Station and the door to the pumping station building. Drive from ORNL parking lot on White Oak Avenue and turn left onto Sixth Street. Continue to the West Portal. Proceed through the gate and turn right. Continue for approximately 0.2 km (0.1 mile) and turn left onto Bethel Valley Road. Drive approximately 3.2 km (2 miles) on Bethel Valley Road to the intersection of Highway 95. Turn right onto Highway 95 and continue to Bear Creek Road; turn left onto Bear Creek Road and drive approximately 5.6 km (3.5 miles). Turn left onto the Gallaher Water Sampling Station road. Continue through the gate for approximately 91 m (100 yd) to GWSS. Lock door and gate upon leaving station.

2. Melton Hill Dam

Proceed from ORNL parking lot on White Oak Avenue. Turn left onto Sixth Street and continue to Central Avenue and through the West Portal. Turn left onto Lagoon Road. At the intersection of Lagoon Road and Highway 95, turn left. Proceed approximately 1.5 miles and turn left onto Melton Hill Dam Road. Continue approximately 0.5 miles and turn left at gates. The water station is on the left behind the switch yard. Key No. 3D-7 will open the door.

3. Kingston

Proceed to the East Gate, turn left, and go through the parking lot. Turn left onto Bethel Valley Road and proceed 2.0 miles to the intersection of Highway 95. Turn right onto Highway 95 and travel 3.4 miles to the intersection of Highways 58/95. Turn left onto Highway 58S and continue 6.6 miles to the intersection of Highways 58/70. Turn right onto Highway 70 and travel 3.9 miles to the second red light in Kingston. Turn left onto Highway 58S and drive 1.1 miles to the Kingston Water Station. The station is on the left behind the South West Apartments.

4. White Oak Dam

Proceed from ORNL parking lot on White Oak Avenue. Turn left onto Sixth Street and continue to Central Avenue through the West Portal. Turn left onto Lagoon Road. At intersection of Lagoon Road and Highway 95, turn left. Proceed approximately 0.5 mile (bypassing PAM 34). White Oak Dam is on the left. Key No. 3D-9 will open the door of the station. Lock the door upon leaving.

5. White Oak Creek

Proceed from the parking lot on White Oak Avenue to Sixth Street. Turn left onto Sixth Street and continue to Central Avenue and through the West Portal. Turn left onto Lagoon Road and continue to the intersection of Lagoon Road and Highway 95. Turn left onto Highway 95 and proceed approximately 0.4 mile (bypassing PAM 34) and turn right onto Jones Island Road. Proceed approximately 1 mile. The White Oak Creek station is on the left near the Clinch River. Key No. 3D-7 will open the door; lock the door upon leaving.

After collecting the water sample, the technician should reverse the directions and return to ORNL.

4.2 Procedure for Determining the Concentration of Radionuclides in Composited Quarterly Water Samples by Ion Exchange Techniques

1. Objective

This procedure is performed to monitor the waterways by concentrating minute quantities of radionuclides via ion exchange chromatography. Elutriants are sent to the Analytical Chemistry Division for spectral and quantitative analysis.

2. Summary

Before collection, the 26-liter jug is cleaned with detergent and rinsed with tap water plus 500 ml of 5M HNO_3. The final rinse is with distilled water; pour 500 ml of distilled water and 70 ml of concd HCl into the jug and deliver to the station. For information on water charts concerning the collection of water at the Gallaher and Melton Hill Water Sampling Stations, see the Appendix. At the Kingston Water Station, the sample jug is exchanged with the attendant who adds 1 liter of untreated water for each day of the collection period. The collection period is once per month for Gallaher and Melton Hill and twice monthly for Kingston. The pH of the sample should be ≤ 1 and adjusted with concd HCL. The pH is readjusted to ≥ 5.0 in the laboratory with sodium hydroxide. One half of the sample is concentrated on the columns, and the other half is evaporated to 150 ml. The bound radionuclides are eluted from the columns with 500 ml 5M nitric acid (HNO_3) and evaporated to 100 ml for spectral and quantitative radionuclide analysis.

3. Reagents

3.1 Nitric acid (HNO_3), 15.9M stock, concentrated

3.2 Hydrochloric acid (HCl), 12M, concentrated

3.3 Anion exchange resin, Dowex-Copolymer 50W, 1 X8, 50-100 mesh)

3.4 Cation exchange resin, Dowex 50 x 8, 50-100 mesh

4. Ion Exchange Column Preparation

4.1 Place Dowex cation or anion resins (at least 300 ml of solid) in distilled H_2O. Stir and allow to swell overnight.

4.2 Aspirate the fluid phase of the resin preparation and resuspend resin in about one-quarter volume of distilled water and allow to settle.

4.3 Acid clean (HCl) the glass column. Stopper the bottom with glass wool and pour a suspension of resin into the column. Allow the resin to settle. Column should contain about 75 ml of resin.

4.4 Connect column to filter and ion exchange assembly for radionuclide concentration procedure. (See Fig. 4.2-1.)

5. Radionuclide Concentration Laboratory Procedure

5.1 Determine the volume of the water sample by:

5.1.1 measuring sample volume with a ruler, and

5.1.2 obtaining the approximate volume in the carboy from the graph (volume in liters per inch in carboy) located on a wall in the water laboratory.

5.2 Remove 2 ml/liter of water sample for tritium analysis and deliver the 2 ml/liter composite sample to the Industrial Safety and Applied Health Physics Division's Bio-Assay Laboratory.

5.3 Adjust pH to 5.0-6.0 with 5M HNO_3.

5.4 Using a vacuum, filter acidified water sample through Whatman No. 42 filter paper (18.5 cm). The vacuum will remove unwanted carbonates that bind to ion exchange columns.

5.5 The sample is passed over the anion resin and the cation resin at a flow rate of approximately 5 ml/min.

5.6 Radionuclides from these columns must be eluted every 50 to 60 liters of flow sample.

5.7 Quarterly elutes containing the radionuclides and their complexes should be taken from the column with 500 ml of 5M HNO_3. (The proper concentration of HNO_3 is essential because a higher concentration can damage the resin.)

5.8 Allow approximately 100 ml of eluate to come off the anion and cation columns (discard eluate). Collect 500 ml of radionuclides

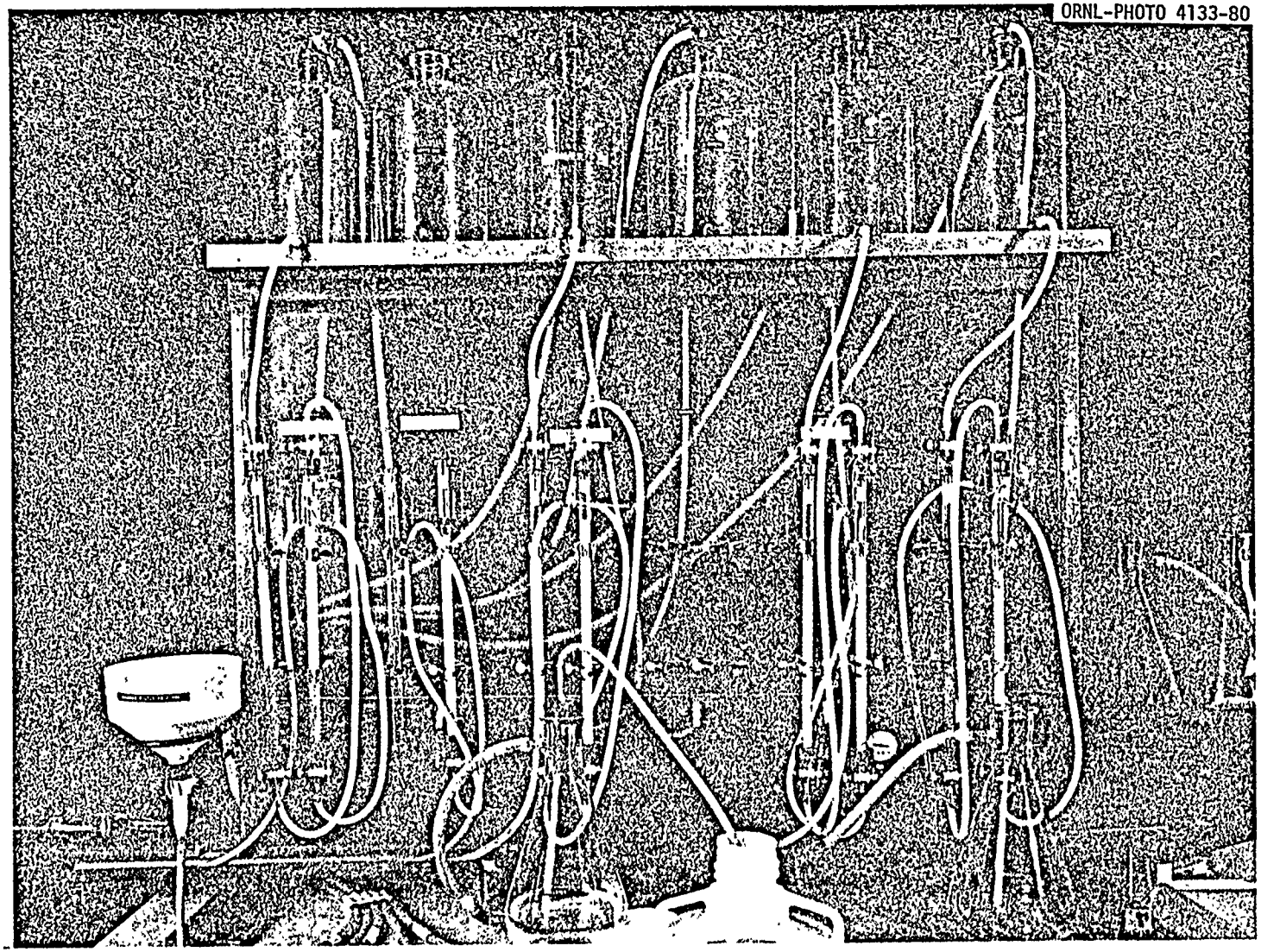

Fig. 4.2-1. Ion exchange columns.

from the columns after the formation of a connection or schlieren type pattern.

5.9 Evaporate the eluate to 100 ml. Transfer sample (eluate) to a clearly labeled 200-ml polyethylene bottle.

5.10 This sample is sent to the Analytical Chemistry Division Laboratory for spectral and quantitative analysis.

5.11 Filters containing sediment and tritium composite water samples should also be submitted.

5.12 Discard the column resin and prepare a new resin bed for the next quarterly composite.

6. Additional Information

6.1 After the acidification of the samples, the molarity of HCl in the total solution should be between 0.01 and 0.02 after this addition.

6.2 Most of the radionuclide activity in water samples occurs in colloidal-size particles. The sample is acidified before being applied to the columns because:

6.2.1 The walls of the container acquire a negative charge, while the colloidal particles that have a higher surface area acquire a positive charge and will electroplate the sides of the container. Acid reduces this interaction.

6.2.2 Carbonates bind effectively to the columns and reduce the bonding of radionuclides to the columns. Acid hydrolyzes the nuclide-releasing carbonates, which are then removed by the vacuum.

6.3 A polystyrene-divinyl benzene cross-linked resin is used with strong acids and bases for the ion exchange chromatography.

4.3 Procedure for Radionuclide Extraction from Rainwater Samples

1. Objective

This procedure is followed to extract and concentrate radionuclides contained in precipitation (rainwater) samples (Fig. 4.3-1). The precipitation collected on the roof of the air monitoring stations flows into a 26-liter polyethylene jug and an overflow jug (Fig. 1.2-1). When collecting the sample, the jug is disconnected from the station, the particles resuspended, and the water poured into a bottle labeled with the date, station, and estimates of water in the carboy. For more information, refer to "Sample Collection at Local and Perimeter Air Monitoring (LAM and PAM) Stations" (Sect. 1.1). The radionuclides contained in these water samples are indications of the activity deposited by washout due to rainfall or precipitation.

2. Summary

The water samples are passed through ion exchange resin columns to extract the radionuclides. The nuclides are "stripped off" the resin with a concentration of 5M nitric acid. The process of "stripping" radionuclides from the charged resin columns is called elution. The eluate (the nitric acid solution containing the radionuclides) is evaporated to dryness on a metal planchet by heating. The planchets are counted for gross-beta radiation. The data are analyzed for indications of nuclide washout from periodic rainfall in the ORNL area.

3. Reagents

3.1 Nitric acid (HNO_3), 15.9M, concentrated

3.2 Cation exchange resin (Dowex 50-8X, 50-100 mesh size)

4. Ion Exchange Column Preparation

4.1 To a container of dry Dowex cation resin, add 300 ml of distilled water. Allow slurry (resin and water) to sit overnight

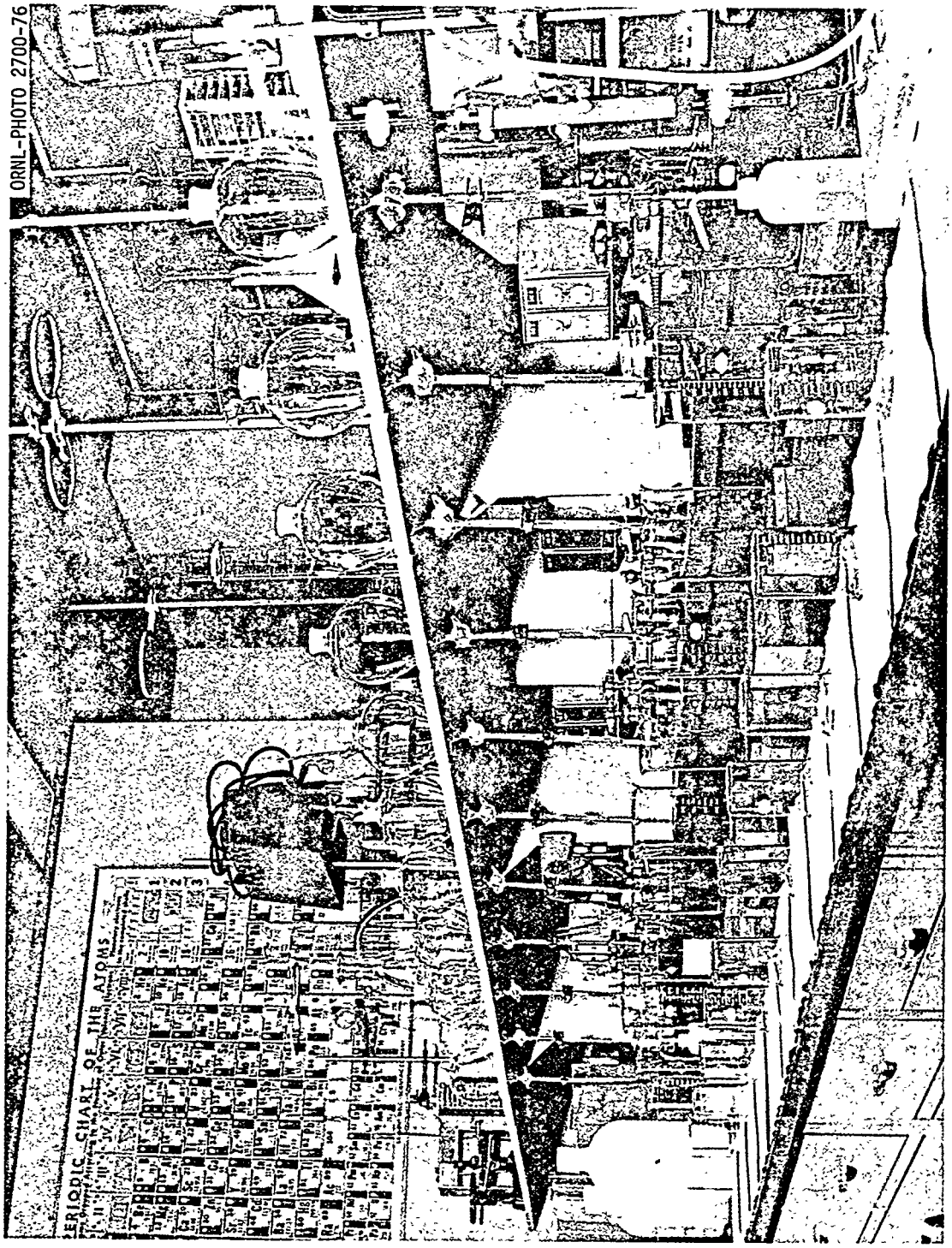

Fig. 4.3-1. Cation columns.

at room temperature so that the water will absorb into the bead-like resin.

4.2 After allowing the resin to settle, carefully pour off water. Add another 300 ml of distilled water to the resin and allow the mixture to settle for 30 min. Repeat this step twice.

4.3 Wash eleven 16.5-mm glass columns and eleven 1000-ml separatory funnels with detergent and tap water, then with isopropyl alcohol, and finally with 6M hydrochloric acid (HCl) (thoroughly rinsing between washes with distilled water).

4.4 Place a small amount of glass wool in the bottom of each glass column and just above the stopcock in the separatory funnels. The glass wool will keep the slurry (prepared in step 4.2) in the column. Each separatory funnel must contain glass wool to trap particulate matter from the rainwater samples.

4.5 Pour 5 ml of cation resin slurry into each glass column. Allow the resin bed to settle into the column.

4.6 Apply stopcock grease to the bottom fixtures of each separatory funnel. Turn the stopcock of the funnel to the off position.

4.7 Connect each prepared ion exchange column to a separatory funnel with a clamp.

4.8 Add 150 ml of distilled water to each separatory funnel, turn the stopcock to the open position, and wash the resin column.

4.9 The columns are now ready for the radionuclide extraction procedure.

5. Radionuclide Extraction from Rainwater Samples

5.1 Carefully pour rainwater sample into the separatory funnel and record date and number of centimeters of water in the 26.0-liter carboy sampler on the Rainfall Data Sheet.

5.2 Obtain the rainfall data (centimeters) from the Rainfall Calibration Graph and record the data on the Rainfall Data Sheet.

5.3 Obtain rainfall data computer cards for each water sample and record the sample dates on and off and total rainfall (in centimeters).

5.4 Turn the stopcock of the separatory funnel to the open position (the flow rate should be about 1 to 2 drops/s). Allow the sample to pass through the resin column.

5.5 Turn the stopcock to the off position and discard the water that has passed through the resin column.

5.6 Obtain a 50-ml glass beaker for each column and label the beaker with the sample number.

5.7 Pour 45 ml of 5M HNO_3 into the separatory funnel; turn the stopcock to the on position, and collect the eluate in the labeled 50-ml glass beaker. The flow rate should be about 1 to 2 drops/s. Do not allow the column to run dry.

5.8 Set beaker containing eluate on the hot plate in the control hood and turn the control on the hot plate to the medium position. Evaporate to dryness.

5.9 With a Pasteur pipette, add approximately 2 ml of 5M HNO_3 to the eluate beaker. Swirl the acid around the beaker to dissolve any nuclides on the sides.

5.10 Transfer this solution to a labeled planchet and evaporate to dryness on the hot plate.

5.11 After the planchets are dry, transfer the planchets and data cards to the planchet carrier. Deliver samples to the counting room for gross-beta analysis.

5.12 The 1-liter bottles used for the LAM stations (rainwater samples) and 50-ml beakers can be reused after washing. The 1-liter bottles used for the RAM stations are discarded.

5.13 All planchets and Pasteur pipettes should be discarded in the appropriate metal- and glass-waste containers, respectively.

4.4 Preparation Procedures for White Oak Dam and Mouth of White Oak Creek Water Samples

Water samples from White Oak Dam (Fig. 4.4-1) and the mouth of White Oak Creek are delivered to the Department of Environmental Management Laboratory on Monday morning for assaying. Samples at White Oak Dam are proportional to the flow over the dam; this is accomplished through the use of a microprocessor computer system (Fig. 4.4-2). The routine preparation includes both weekly and monthly procedures.

1. Weekly Procedures

1.1 White Oak Dam

1.1.1 The technician should carry to the site of collection an 8-liter jug, a 1-liter bottle, and key no. 9 (to unlock station). Inside the station are three barrels. Water should be collected from the center barrel. Before collection, the level of water in the barrel is measured with a ruler. The level of water, date of collection, time, and initials of the collector are recorded on the jug and bottle. The water in the center barrel is stirred and collected from the spout of the barrel. The excess water is discarded into the drain.

1.1.2 The Geiger-Miller (GM) tubes are submerged in the water between the gate and station. The GM tubes are removed from the water, cleaned with a brush, and submerged again. A box (shelter) on the platform above the dam houses the flow charts. The flowchart should be removed and labeled with the data, location, time off, and the technician's initials. NOTE: The chart (located in the box) is very difficult to exchange; therefore, it is feasible to seek help from a trained technician. The lake height and scale height are also read and recorded in a log book inside the station. The technician should lock the gate when leaving.

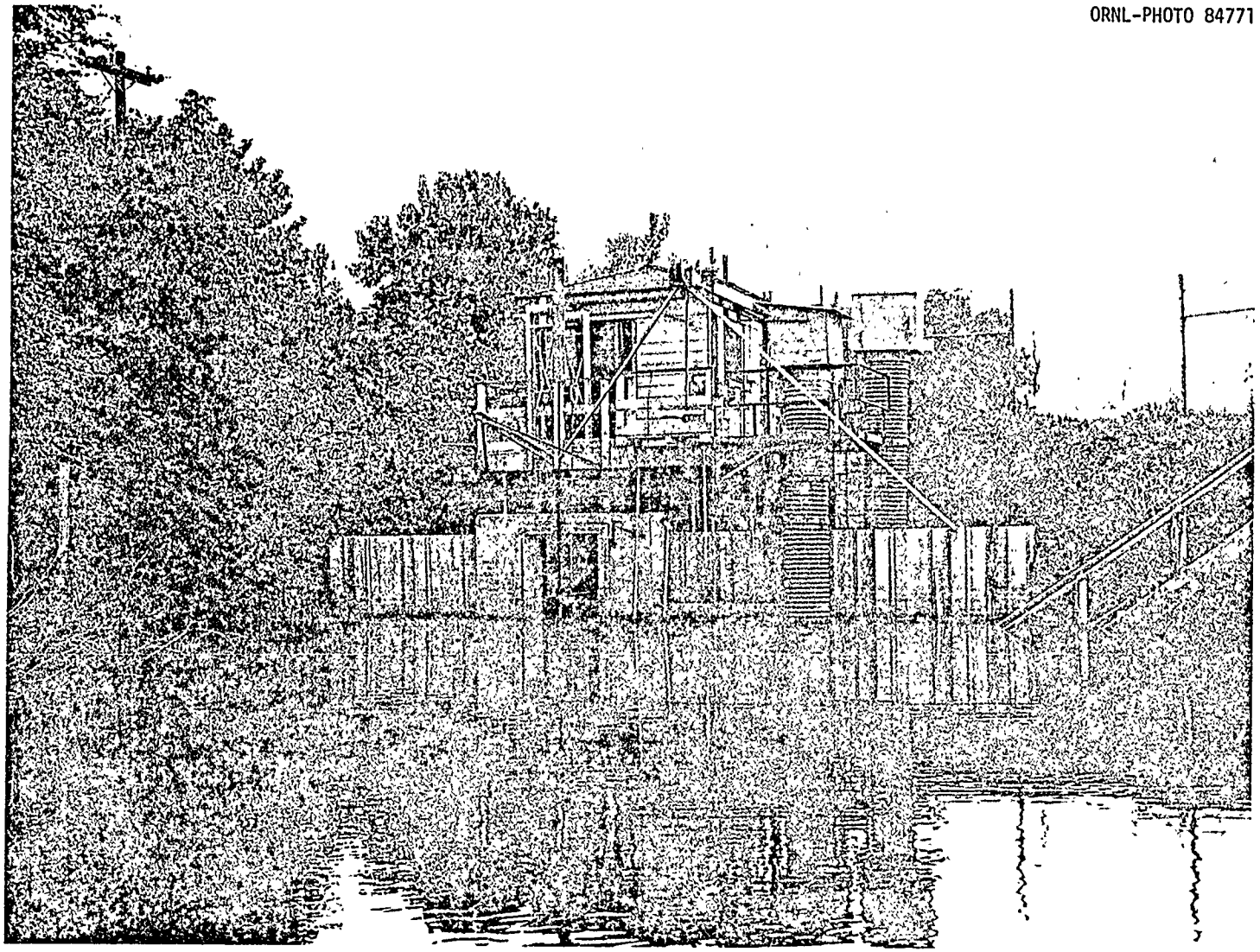

Fig. 4.4-1. White Oak Dam.

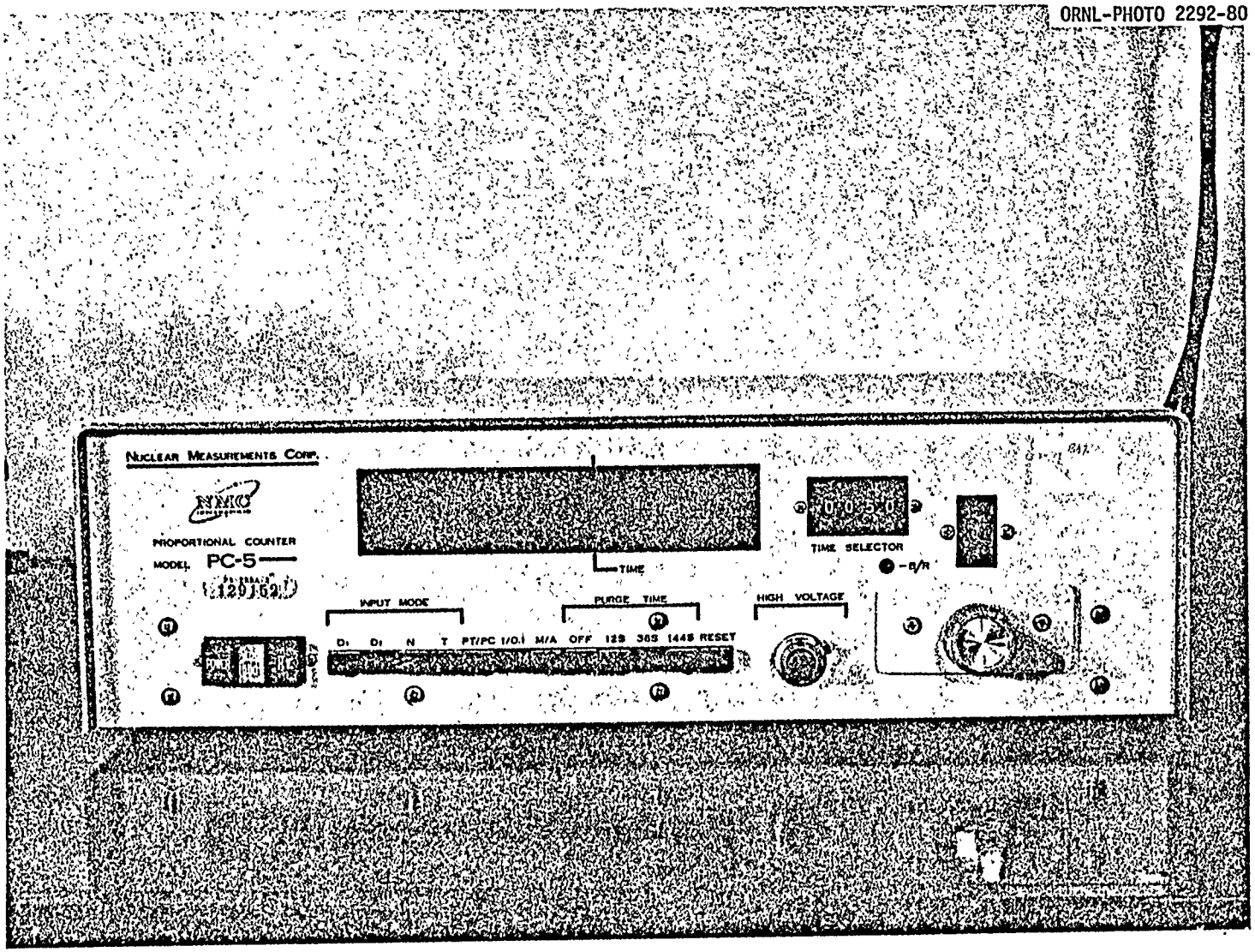

Fig. 4.4-2. Panel of microprocessor system.

1.1.3 Take three 50-ml samples from the water jug and evaporate to dryness in 10-ml aluminum planchets. The planchets are counted for gross-beta activity with a GM counter. The efficiency of this counter is approximately 9% with a background counting rate of 8 counts/min. The average net count rate (counts min^{-1} ml^{-1}) is reported to the shift supervisor at the end of the day. A permanent record is kept for future reference.

1.1.4 Deliver a 1-liter and a 140-ml sample to the Industrial Safety and Applied Health Physics Division Bio-Assay Laboratory for plutonium, transplutonium, and tritium analyses.

1.1.5 Deliver a 2-liter sample to the Low-Level Laboratory in the Analytical Chemistry Division for quantitative analyses for strontium and gross alpha.

1.1.6 Save the remaining portion of the weekly sample for a monthly composite. Do not combine these samples at this time.

1.2 Mouth of White Oak Creek

1.2.1 The technician should carry an 8-liter jug and key No. 7 to the station. The amount of water in the jug should be measured with a ruler and recorded on the sample jug. The date and station should also be recorded on the jug. The water is stirred and collected from the spout of the jug. Excess water is discarded and the station is locked upon leaving.

1.2.2 Deliver a 140-ml sample to the Bio-Assay Laboratory for tritium analysis.

1.2.3 Save the remaining portion of the water for a monthly composite. To make the composite sample from White Oak Creek, pour 4 liters of water from each weekly sample

into a jug and add 100 ml of 4M HCl. The total composite sample volume is approximately 16 liters.

2. Monthly Procedures

2.1 White Oak Dam

2.1.1 Combine the weekly samples proportionally to the weekly flow of water passing through the dam so that a total monthly composite of 16 liters is available for assaying. This may be calculated with the use of the continuously monitoring flow charts which record the daily flow of water through the dam. Accurate records of the weekly and monthly flow of water through the dam is thus recorded. To determine the amount of water to use from each weekly sample (for the monthly composite), the total weekly flow of water is divided by the total monthly flow of water through the dam. This proportion is multiplied by the number of milliliters of water desired for the monthly composite (16,000 ml or 16 liters).

$$\text{Total weekly flow} = 41.9 \times 10^{10} \text{ ml}$$

$$\text{Total monthly flow} = 104.97 \times 10^{10} \text{ ml}$$

$$\text{Total monthly composite desired} = 16{,}000 \text{ ml}$$

$$\frac{41.9 \times 10^{10} \text{ ml}}{104.97 \times 10^{10} \text{ ml}} \times 16{,}000 \text{ ml} = 6387 \text{ ml}$$

The number of milliliters of water calculated for each week is added to the monthly composite jug.

2.1.2 Deliver a 1-liter and a 140-ml sample of the monthly composite to the Bio-Assay Laboratory for plutonium, transplutonium, and tritium analyses. Also deliver a 1-liter sample of the monthly composite to the Analytical Chemistry Division Low-Level Laboratory for tritium analysis. The data can be confirmed by comparing the results from Analytical Chemistry and the Bio-Assay Laboratories.

2.1.3 To 6 liters of the composite sample, add 25 ml of concd HNO_3. Evaporate the sample to 150 ml and deliver to Analytical Chemistry for quantitative assaying of radionuclides by gamma spectrometric techniques. The sample is sent to the Low-Level Analytical Chemistry Laboratory for the determination of radiostrontium content and gross-beta activity.

2.2 Mouth of White Oak Creek

2.2.1 Deliver a 140-ml sample and a 1-liter sample of the monthly composite to the Bio-Assay Laboratory and the Analytical Chemistry Division Laboratory, respectively, for tritium analysis.

2.2.2 To 6 liters of the monthly composite sample, add 25 ml of concd HNO_3. Evaporate sample to 150 ml and deliver to Analytical Chemistry Division (Special Project Laboratory) for quantitative assaying of radionuclides by gamma spectrometric techniques. The sample is sent to the Low Level Analytical Chemistry Laboratory to determine the radiostrontium content and gross-beta activity.

4.5 Determining Iodine Activity in Aqueous Solutions (performed by Analytical Chemistry Division Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope

This method is applicable to the determination of iodine in aqueous solutions. The two most important iodine isotopes determined are iodine-131 and, with modifications, iodine-129.

2. Summary

Iodine activity is separated from other fission products by oxidation to periodate with sodium hypochlorite in basic solution, followed by reduction of the periodate to iodine with hydroxylamine hydrochloride and extraction of the iodine into carbon tetrachloride. The iodine is removed from the carbon tetrachloride by extraction into water that contains sodium bisulfite. It is then purified by another carbon tetrachloride extraction cycle using sodium nitrite for the oxidation of iodide to iodine and using sodium bisulfite for the reduction of iodine to iodide. The iodide is finally precipitated as silver iodide, washed with ethanol and ether, and then air dried, weighed, and mounted. The iodine activity is counted in a low-background beta counter. The oxidation of iodide to periodate with sodium hypochlorite in a basic solution ensures complete interchange of radioiodine with the carrier.

3. Status

The relative standard error of the method is thought to be ±5%. Contamination of the iodine activity by other fission activities is negligible.

Iodine activity in the form of free iodine in organic samples is determined by this method. The behavior of the oxidized states of iodine in organic samples has not been investigated. However, analyses of organic streams that contain iodine-131 are currently being made with excellent recovery of the activity. The chemical

yield is 80% or better, and the time required for a complete analysis is 45 to 60 min. Iodine-129 analyses require more extensive treatment with a resultant longer analysis time.

4. Apparatus

4.1 Separatory funnels, 1-liter

4.2 Glass extraction vials, 50-ml

5. Reagents

5.1 Sodium hypochlorite (NaOCl) solution, approximately 5% NaOCl

5.2 Sodium nitrate ($NaNO_2$) solution, approximately 1M $NaNO_2$. Prepare by dissolving 69 g of $NaNO_2$ in 1 liter of distilled water.

5.3 Carbon tetrachloride (CCl_4)

5.4 Sodium carbonate (Na_2CO_3), 2M

5.5 Nitric acid (HNO_3), concentrated

5.6 Hydroxylamine hydrochloride ($NH_2OH \cdot HCl$), 1M

5.7 Sodium bisulfite ($NaHSO_3$), 1M

5.8 Nitric acid (HNO_3), 6M

5.9 Silver nitrate ($AgNO_3$), 0.1M

6. Safety

CAUTION: Carbon tetrachloride is a toxic substance.

7. Sampling

Measure at least 250 ml of water samples.

8. Procedure

8.1 Interchange of iodine with carrier

8.1.1 Place 10 ml of 2M Na_2CO_3 solution and 2 ml of iodine carrier in a 500-ml separatory funnel. Pipette into the funnel approximately 250 ml of the sample. Record the volume of the sample taken. Add 2 ml of 5% NaOCl solution. Swirl to mix. Acidify the solution by adding slowly 3 to 4 ml of concd HNO_3. Add 3 to 5 ml of 1M $NH_2OH \cdot HCl$ solution and 25 ml of CCl_4. Extract the iodine into the CCl_4. Draw off the CCl_4 layer into a new separatory funnel, then discard the aqueous layer.

8.1.2 Back-extract the iodine from the CCl_4 layer with 10 ml of H_2O that contains 3 to 5 drops of 1M $NaHSO_3$ solution until both phases are colorless, then discard the CCl_4.

8.1.3 To determine iodine-129, encapsulate the aqueous solution and irradiate with iodine-129 standard for $\geq$0.5 h at 10^{12} ncm^{-2} s^{-1}, then determine iodine-130 following the procedures in step 9.

9. Determination of iodine activity

9.1 Add 1 ml of 6M HNO_3 solution, 3 to 5 drops of 1M $NaNO_2$ solution, and 10 ml of CCl_4. Extract the iodine into the CCl_4, draw off the CCl_4 layer into a new separatory funnel and discard the aqueous layer.

9.2 Shake the CCl_4 layer with 10 ml of H_2O that contains 3 to 5 drops of 1M $NaHSO_3$ solution until both phases are colorless. Discard the CCl_4 layer and drain the aqueous layer into a 50-ml glass centrifuge tube.

9.3 Acidify the solution with 1 ml of 6M HNO_3 solution and heat the solution nearly to boiling.* Add by drops 2 ml of 0.1M $AgNO_3$ solution. Digest the precipitate of AgI with occasional stirring.†

9.4 Weigh a 25-mm watch glass together with a Whatman No. 40 filter paper disk of 1.7-cm diameter and record the tare in grams on a data card. Place the filter paper in a Hirsch funnel and apply suction. Transfer the precipitate onto the tared filter paper disk.

9.5 Wash the precipitate three times with H_2O, three times with ethanol, and three times with ether. Dry by allowing suction to continue for 1 min.

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*The purpose of the acidification and heating is to expel SO_2 which might interfere in the AgI precipitation.

†AgI tends to form both a milky suspension and large clumps of precipitate. The digestion procedure aids in coagulating the suspension and and also in breaking up the large particles of precipitate.

9.6 Place the precipitate and paper on the 25-mm watch glass. Weigh and record the total weight in grams on the data card as gross weight.

9.7 Calculate the net weight of the AgI precipitate.

9.8 Mount the precipitate for counting.

Working Bibliography for Sect. 4.5

D. N. Hume, N. E. Ballou, and L. E. Glendenin, "Iodine, Hypochlorite-Hydroxylamine Method," *A Manual of the Radiochemical Determination of Fission Product Activities*, CN-2815, pp. 45-47 (June 30, 1945).

B. H. Ketelle, H. Zeldres, A. R. Brosi, and R. A. Dandl, "Gamma-Coincident Beta-Spectra of ^{131}I," *Phys. Rev.*, 84, 585 (1951).

S. A. Reynolds, "Routine Methods of Radioisotope Analysis," ORNL-256, Sect. II, p. 2 (July 23, 1948).

4.6 Radiochemical Method for Determining Strontium in Water (performed by Analytical Chemistry Division Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

This method is applicable to the determination of strontium-90 in potable, natural, and industrial waters.

2. Summary of Method

2.1 Strontium carrier is equilibrated with the sample, precipitated as the insoluble carbonate, and separated from calcium and magnesium by nitrate precipitations followed by acetone washes. Further precipitation is accomplished by removing impurities with hydroxide scavenging and by removing barium as the chromate. Final purification is made by precipitation of strontium as the oxalate, which is mounted for beta counting. The sample is counted on a low-background beta counter.

2.2 The lowest reported concentration is 7.4×10^{-4} Bq/ml (2×10^{-2} pCi/ml) for a 1-liter sample aliquot.

3. Sample Handling and Preservation

3.1 Samples are adjusted to a pH of 1 with nitric acid as soon as practicable unless suspended and/or soluble strontium determinations are needed, in which case the samples are filtered before being adjusted with acid.

3.2 After preliminary treatment, the samples are stored in either glass or plastic containers.

4. Interferences

4.1 Strontium-89, when present in the sample, interferes with the beta counting of strontium-90. The presence of strontium-89 can be ascertained by absorption studies, and its interference can be circumvented by indirect determination of strontium-90 via the yttrium-90 daughter after adequate ingrowth.

4.2 Due to self-absorption, the counting efficiency for strontium-90 varies with the amount of solids which are counted on the mounts.

5. Apparatus

5.1 Lab glassware

5.1.1 Beakers, size adequate for sample aliquot

5.1.2 Centrifuge tubes, 50-ml glass

5.2 Centrifuge

5.3 Hot plate

5.4 Ice bath

5.5 Filter paper, Whatman No. 541 (11-cm)

5.6 Filter paper, Whatman No. 1 (18-mm)

5.7 Analytical balance

5.8 Filter flask and funnel

5.9 Fritted-glass filter crucibles

5.10 Desiccator

5.11 Low-background beta counter

6. Reagents

6.1 Acetic acid, 6M: Add 340 ml of glacial acetic acid (CH_3COOH) to 500 ml of water and dilute to 1 liter with water.

6.2 Ammonium acetate solution, 6M: Dissolve 462 g of ammonium acetate ($NH_4C_2H_3O_2$) in 500 ml of water and dilute to 1 liter with water.

6.3 Sodium carbonate solution, 2M: Dissolve 248 g of sodium carbonate monohydrate ($Na_2CO_3 \cdot H_2O$) in 700 ml of water and dilute to 1 liter with water.

6.4 Ammonium oxalate solution, saturated: Add 200 g of ammonium oxalate monohydrate [$(NH_4)_2C_2O_4 \cdot H_2O$] to 500 ml of water in a 1-liter container, dilute to 1 liter with water, mix thoroughly, and let stand overnight before using.

6.5 Sodium chromate solution, 1.5M: Dissolve 176 g of sodium chromate tetrahydrate ($Na_2CrO_4 \cdot 4H_2O$) in water and dilute to 500 ml with water.

6.6 Barium carrier solution, 10 mg Ba/ml: Dissolve 19.0 g of barium nitrate [$Ba(NO_3)_2$] in water and dilute to 1 liter with water.

6.7 Nitric acid (HNO_3), fuming

6.8 Ferric nitrate solution, 50%: Dissolve 100 g of ferric nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$] in water and dilute to 100 ml with water.

6.9 Ferric nitrate solution, 0.1M: Dissolve 40.4 g of ferric nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$] in water and dilute to 1 liter with water.

6.10 Nitric acid, 6M: Add 375 ml of concd HNO_3 to 500 ml of water and dilute to 1 liter with water.

6.11 Acetone

6.12 Sodium hydroxide solution, 19M: Slowly add 760 g of sodium hydroxide (NaOH) to 500 ml of water and dilute to 1 liter with water. Store in a plastic container.

6.13 Ethyl alcohol (C_2H_5OH), 95%

6.14 Diethyl ether ($C_2H_5OC_2H_5$), anhydrous

6.15 Ammonium hydroxide (NH_4OH), concentrated

6.16 Strontium carrier solution: Dissolve 27.3 g of strontium nitrate [$Sr(NO_3)_2$] in a minimum of HNO_3 and dilute to 1 liter with water.

6.16.1 Standardization of strontium carrier: Pipette 5.00 ml of strontium carrier solution into a 100-ml beaker and add 30 ml of water. Adjust the pH to 9 with concd NH_4OH, add 10 ml of saturated $(NH_4)_2C_2O_4$ solution, and heat to nearly boiling with stirring. Cool to room temperature and quantitatively transfer the precipitate to a previously tared filter crucible with hot water. Wash the precipitate several times with hot water, three times with 10-ml portions of ethyl alcohol, and two times with 10-ml portions of diethyl ether. Desiccate the crucible and precipitate under vacuum to a constant weight. The net weight is the weight of strontium

oxalate monohydrate ($SrC_2O_4 \cdot H_2O$) in 5.00 ml of the strontium carrier solution.

6.17 Phenolphthalein indicator solution, 5%. Dissolve 5 g of phenolphthalein ($C_{20}H_{14}O_4$) in 50 ml of 95% ethyl alcohol and dilute to 100 ml with water.

7. Procedure

7.1 Transfer a measured volume of the sample to an adequately sized beaker and adjust to a pH of 1 with nitric acid if not previously adjusted.

7.2 Add 1.00 ml of the standardized strontium carrier solution and 1 ml of 50% ferric nitrate solution.

7.3 Place on a hot plate and heat with stirring to near boiling. Digest for 20 min.

7.4 Cautiously add 19M NaOH, with stirring, to a pH of 10.

7.5 Add 50 ml of 2M Na_2CO_3 solution and continue to digest on the hot plate with stirring for 30 min.

7.6 Remove from the hot plate and allow the precipitate to settle overnight.

7.7 Decant the supernatant liquid and discard it.

7.8 Transfer the precipitate to a 50-ml glass centrifuge tube, centrifuge for 5 min at 1500 rpm, and discard the supernatant liquid.

7.9 Wash the precipitate with 30 ml of water, centrifuge, and discard the water wash solution.

7.10 Dissolve the precipitate in a minimum of concd HNO_3, and then add 25 ml of fuming HNO_3.

7.11 Place the tube in an ice bath and stir the solution until precipitation is complete.

7.12 Remove the tube from the ice bath and centrifuge at 1500 rpm for 5 min. Decant the supernatant solution into a large volume of water and discard. Drain the tube completely (leaving a minimum of HNO_3) as a precaution against any adverse reaction with the acetone wash which follows.

7.13 Add 30 ml of acetone and wash the precipitate thoroughly while stirring.

7.14 Centrifuge for 5 min at 1500 rpm and decant the acetone wash solution into a clearly marked organic-waste container.

7.15 Dissolve the precipitate in a minimum of water.

7.16 Repeat steps 7.10 through 7.14 starting with the addition of fuming HNO_3 in step 7.10.

7.17 Dissolve the precipitate in 10 ml of water.

7.18 Add two drops of phenolphthalein indicator solution and 0.5 ml of 0.1M $Fe(NO_3)_3$ solution.

7.19 Add concd NH_4OH by drops, with stirring, until the phenolphthalein end point is reached, then add five more drops.

7.20 Centrifuge for 5 min at 1500 rpm.

7.21 Filter the supernatant solution through Whatman No. 541 filter paper into another 50-ml glass centrifuge tube; discard the precipitate. Record the time in which the filtering is done as the separation time of strontium-90 from yttrium-90. Wash the filter with 3 ml of water.

7.22 Neutralize the solution with 6M HNO_3; then add 1 ml of 6M acetic acid, 2 ml of 6M ammonium acetate, and 1 ml of barium carrier.

7.23 Heat the solution to near boiling; then add 1.5M Na_2CrO_4 solution by drops, with stirring, to precipitate barium chromate. Chill in an ice bath and stir to complete the precipitation. Check for complete precipitation of barium by adding a few more drops of Na_2CrO_4.

7.24 Centrifuge for 5 min at 1500 rpm.

7.25 Filter the supernatant solution through Whatman No. 541 filter paper into another 50-ml glass centrifuge tube and wash the filter with 3 ml of water. Discard the precipitate.

7.26 Add 2 ml of concd NH_4OH to solution and heat to boiling.

7.27 Add 5 ml of saturated ammonium oxalate solution, with stirring, to precipitate the strontium oxalate.

7.28 Chill in an ice bath and continue to stir to complete the precipitation.

7.29 Centrifuge for 5 min at 1500 rpm and discard the supernatant solution.

7.30 Place a tared 18-mm filter paper in the filtering funnel and wet with water using a vacuum on the filtering flask.

7.31 Transfer the precipitate onto the filter with hot water; then wash with two 10-ml portions of hot water, three 5-ml portions of 95% ethyl alcohol, and two 5-ml portions of diethyl ether.

7.32 Weigh the filter paper and precipitate, determine the chemical recovery, and mount for beta counting.

7.33 Immediately count the sample mount on a low-background beta counter.

8. Calculations

$$^{90}Sr = ABVM/DV \ , \quad Bq/m^3 \ ,$$

where

A = net counts per minute of purified ^{90}Sr,

B = efficiency factor for ^{90}Sr, including self-absorption correction,

D = fraction of strontium carrier recovered,

V = volume of sample, ml,

M = conversion factor to Bq; 1 Bq = 60 dis/min.

9. Precision and Accuracy

The precision at the 95% confidence level is ±12%. The method exhibits a negative bias of 5% when applied to controls of known strontium-90 concentration.

Working Bibliography for Sect. 4.6

M. A. Franson (ed.), *Standard Methods for Examination of Water and Waste Water*, 14th ed., 1976.

J, Kooi, "Quantitative Determination of Strontium-89 and Strontium-90 in Water," *Anal. Chem.*, 30, 532 (1958).

R. B. Hahn and C. P. Straub, "Determination of Radioactive Strontium and Barium in Water," *J. Am. Water Works Assoc.*, 47, No. 4, 335 (1955).

4.7 Radiochemical Method for Determining Radium-226 in Water (performed by Analytical Chemistry Division Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope

This method is applicable to the determination of radium-226 in leach solutions of ores and minerals and in water samples.

2. Summary

Radium is precipitated with the lead nitrate-barium nitrate and lead sulfate-barium sulfate. Selective dissolution of barium sulfate-radium sulfate is made with EDTA. Reprecipitated barium sulfate-radium sulfate is dried on a steel plate for alpha counting.

3. Status

Count rates observed over a period of days permit observance of daughter growth and better counting statistics. Consideration must be given to the ratio of radium to barium in the sulfate precipitation step. A radiochemical yield for barium is measured using barium-133 tracer.

4. Apparatus

4.1 Centrifuge tubes, 50-ml glass

4.2 Centrifuge cone, 15-ml conical

5. Reagents

5.1 Nitric acid (HNO_3), 90%

5.2 Lead nitrate [$Pb(NO_3)_2$] solution, 10 mg/ml

5.3 Barium solution, 1 mg/ml

5.4 EDTA solution, 0.25M disodium salt

5.5 Acetic acid (CH_3COOH), glacial

5.6 Ammonium hydroxide (NH_4OH), 6N and 15N

5.7 Methyl orange indicator

5.8 Barium-133 tracer, 1000 counts min^{-1} ml^{-1}

5.9 Sulfuric acid (H_2SO_4), 1:1, 18N

6. Procedure

6.1 Pipette a test aliquot of the sample into a centrifuge tube. Add 1 ml of lead solution, 1 ml of the barium solution, and 1 ml of the tracer solution.

6.2 Add 20 ml of 90% HNO_3. Cool in an ice bath.

6.3 Cautiously transfer the tubes to a centrifuge and centrifuge for 5 min. Carefully decant the acidic supernatant solution. Wash the precipitate with acetone if calcium content is high.

6.4 Dissolve the precipitate in water. Heat to boiling and add methyl orange indicator and 1:1 H_2SO_4 to a pink color, then add 0.3 ml excess.

6.5 Digest for 10 min. Let settle for about 30 min.

6.6 Centrifuge for 5 min and wash the precipitate with dilute HNO_3, discarding the wash solution.

6.7 Dissolve the precipitate in 4 ml of water and 4 ml of EDTA; add 1.2 ml of 6N NH_4OH. Warm the solution, then add by drops about 1 ml of glacial acetic acid. Digest 10 min, centrifuge, and discard the supernatant solution.

6.8 Wash the precipitate with water, discard the wash solution, and transfer the material to a steel plate. Spread the material over the disk area. Dry and flame the disk.

6.9 Observe a gross-alpha count. Pulse analyzes the source, and hold for recount. During the holding period, determine the chemical yield of barium-133.

6.10 With the appropriate proportionality constant for radium to barium (D or λ), calculate the true radium yield.

Working Bibliography for Sect. 4.7

J. H. Harley (ed.), *HASL Procedures Manual*, Health and Safety Laboratory, HASL-300, August 1974.

Radium-226 Analysis Principles, Interference and Practice, National Lead Company, Inc., WIN-112, February 1, 1960.

P. E. Trujillo, Jr., *Analytical Procedures for the Determination of Radionuclides in Air Filters, Water, and Soils,* Los Alamos Scientific Laboratory, H8-MR-72-3, May 1972.

4.8 Radiochemical Method for Determining Uranium in Water (performed by Analytical Chemistry Division Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

This method is applicable to the determination of uranium in potable, natural, and industrial waters.

2. Summary of Method

2.1 The sample is equilibrated with uranium-232, which is used as an internal standard. Uranium is subsequently purified chemically by use of anion exchange resin chromatography and repeated methyl isobutyl ketone (hexone) extractions. The extracted uranium is deposited on a stainless steel disk and counted on a multichannel analyzer using a silicon surface-barrier detector to determine the uranium concentration.

2.2 The lowest reported concentration is 7.4×10^{-6} Bq/ml (2×10^{-4} pCi/ml) for a 1-liter sample.

3. Sample Handling and Preservation

3.1 If suspended and/or soluble uranium determinations are desired, the samples should first be filtered to remove the suspended particulates as soon as practicable; the samples should immediately be adjusted to a pH of 1 with nitric acid (HNO_3).

3.2 If total uranium determinations are desired, the samples should be adjusted to a pH of 1 as soon as practicable without filtering.

3.3 After pH adjustments, the samples are stored in either glass or plastic containers.

4. Interferences

4.1 Iron in milligrams per milliliter concentrations tends to follow uranium throughout the chemistry causing serious degradation of alpha measurements.

4.2 Alpha pulse-height analysis eliminates interferences from other alpha emitters.

5. Apparatus

5.1 Glass ion exchange column, 8-mm ID by 25-cm long fitted with a stopcock and reservoir

5.2 Centrifuge

5.3 Vortex mixer

5.4 Hot plate

5.5 Stainless steel disks

5.6 Extraction vials, 50-ml with plastic-lined screw caps

5.7 Transfer pipettes

5.8 Beakers, 100-ml, 250-ml, and a size to accommodate sample aliquot

5.9 Multichannel analyzer system with silicon surface-barrier detector(s)

6. Reagents

6.1 Nitric acid (HNO_3), concentrated

6.2 Nitric acid (HNO_3), 8M: Add 500 ml of concd HNO_3 to 500 ml of water.

6.3 Aluminum nitrate solution, 2.8M: Dissolve 1050 g of aluminum nitrate nonahydrate [$Al(NO_3)_3 \cdot 9H_2O$] with heat in a minimum of water. Cautiously add 100 ml of concd NH_4OH with stirring. Continue heating and stirring until all of the precipitate dissolves, then dilute to 1 liter with water.

6.4 Sodium nitrite ($NaNO_2$), crystals

6.5 Methyl isobutyl ketone (hexone)

6.6 Potassium bromate ($KBrO_3$), crystals

6.7 Uranium-232 tracer solution: Dilute a stock solution of uranium-232 to a concentration of 10 dis min^{-1} ml^{-1}.

6.8 Anion exchange resin: Dowex 1-X4 (50-100 mesh, chloride form) or equivalent.

7. Procedure

7.1 Transfer a measured aliquot of the sample to an adequately sized beaker.

7.2 Add 1 ml of 10 dis min^{-1} ml^{-1} uranium-232 solution.

7.3 Place on a hot plate covered with an asbestos mat and dry.

7.4 Dissolve the residue in 25 ml of 8M HNO_3.

7.5 Add 0.5 g of $NaNO_2$ crystals and heat to boiling.

7.6 Remove from heat and allow 20 min digestion time.

7.7 While the sample is digesting, prepare a resin column as follows:

7.7.1 Place a glass-wool plug in the bottom of the column described in step 5.1.

7.7.2 Slurry the resin (see step 6.8) with water and immediately discard the fines by decanting. Repeat as necessary until fines are removed.

7.7.3 Transfer 4 ml of the resin to the column with water. Prevent any channeling by maintaining the solution level above the resin using the stopcock.

7.7.4 Place a glass-wool plug on top of the resin.

7.7.5 Convert the resin to the nitrate form by passing several column volumes of 8M HNO_3 through the column until the resin is free of chloride ions.

7.8 Transfer the sample solution, which should be at room temperature, to the prepared resin column.

7.9 Place a 250-ml beaker beneath the column and allow the sample solution to drain into the beaker at a flow rate of 2 ml/min.

7.10 Rinse the beaker with 25 ml of 8M HNO_3 and transfer the rinse to the column.

7.11 Allow the rinse to drain into the beaker also.

7.12 Place the beaker containing the column effluent on a hot plate and take to dryness.

7.13 Dissolve the residue in 10 ml of $Al(NO_3)_3$ solution and transfer to an extraction vial using a minimum of $Al(NO_3)_3$ to rinse the beaker.

7.14 Add an equal volume of hexone and extract on a Vortex mixer for 10 min.

7.15 Centrifuge for 2 min to separate the phases and discard the aqueous phase.

7.16 Add an equal volume of water and back-extract into the water on a Vortex mixer for 10 min.

7.17 Centrifuge for 2 min to separate the phases.

7.18 Transfer the aqueous phase to a 100-ml beaker.

7.19 Repeat steps 7.16, 7.17, and 7.18.

7.20 Place the beaker containing the water stripped solution on a hot plate and take to dryness.

7.21 Add enough 8M HNO_3 to moisten the residue.

7.22 Add 10 to 20 mg of $KBrO_3$ crystals and digest for 10 min.

7.23 Dissolve and transfer the residue to an extraction vial with 5 ml of $Al(NO_3)_3$ solution.

7.24 Repeat step 7.14 using 1 ml of hexone; repeat step 7.15.

7.25 Transfer the entire hexone extract by drops to a stainless steel disk placed on a hot plate set at 100°C.

7.26 Flame the disk to a red heat.

7.27 Measure the uranium alpha activities by pulsing with a silicon surface-barrier detector and multichannel analyzer.

8. Calculations

$$^{238}U = AEM/DV \quad , \quad Bq/m^3 \ ,$$
$$^{235}U = BEM/DV \quad , \quad Bq/m^3 \ ,$$
$$^{234}U = CEM/DV \quad , \quad Bq/m^3 \ ,$$

where

A = net integrated counts of ^{238}U from pulse analysis,
B = net integrated counts of ^{235}U from pulse analysis,
C = net integrated counts of ^{234}U from pulse analysis,
D = net integrated counts of ^{232}U from pulse analysis,
E = dis/min of ^{232}U tracer added,
V = volume of sample, ml,
M = conversion factor to Bq; 1 Bq = 60 dis/min.

9. Precision and Accuracy

9.1 The precision is estimated to be ±15%.

Working Bibliography for Sect. 4.8

J. E. Grindler, *The Radiochemistry of Uranium*, NAS-NS 3050, March 1962.

F. B. Johns (ed.), *Handbook of Radiochemical Analytical Methods*, EPA-680/4-75-001, February 1975.

4.9 Radiochemical Method for Determining Plutonium in Water (performed by Analytical Chemistry Division Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

This method is applicable to the determination of plutonium in potable, natural, and industrial waters.

2. Summary of Method

2.1 The plutonium in the sample is equilibrated with plutonium-242 tracer, coprecipitated with bismuth phosphate, adsorbed on anion exchange resin, selectively eluted from the resin, coprecipitated with praseodymium hydroxide, and extracted with thenoyltrifluoroacetone-xylene. The plutonium extract is dried on a stainless steel disk. Alpha pulse-height analysis is used to determine plutonium on the counting disk.

2.2 The lowest reported concentration is 7.4×10^{-6} Bq/ml (2×10^{-4} pCi/ml) for 1-liter samples.

3. Sample Handling and Preservation

3.1 If suspended and/or soluble plutonium determinations are desired, the samples should first be filtered to remove the suspended particulates as soon as practicable; then the samples should immediately be adjusted to a pH of 1 with nitric acid.

3.2 If total plutonium determinations are desired, the samples should be adjusted to a pH of 1 with nitric acid as soon as practicable without filtering.

3.3 After preliminary treatment, the samples are stored in either glass or plastic containers.

4. Interferences

4.1 Interferences from other alpha-emitting nuclides are generally eliminated by alpha pulse-height analysis except for plutonium-240, which cannot be resolved from plutonium-239. Mass spectrometric analysis is required if both of these isotopes are desired.

5. Apparatus

5.1 Glass ion exchange column, 8-mm ID by 25-cm long fitted with a stopcock and reservoir

5.2 Hot plate

5.3 Centrifuge

5.4 Vortex mixer

5.5 Extraction vials, 50-ml with plastic-lined caps

5.6 Lab glassware

5.6.1 Beakers, to accommodate sample aliquot, and 250-ml size

5.6.2 Centrifuge tubes, 50-ml glass, 100-ml glass, and plastic

5.7 Transfer pipettes

5.8 Stainless steel discs

5.9 Multichannel analyzer system with silicon surface-barrier detector(s)

6. Reagents

6.1 Nitric acid (HNO_3), concentrated

6.2 Nitric acid (HNO_3), 8M: Add 500 ml of concd HNO_3 to 500 ml of water.

6.3 Bismuth nitrate solution [$Bi(NO_3)_3$], 0.1M: Dissolve 20.9 g of bismuth metal in HNO_3 and dilute to 1 liter with 8M HNO_3.

6.4 Phosphoric acid (H_3PO_4), concentrated.

6.5 Ammonium hydroxide [$NH_4(OH)$], concentrated.

6.6 Plutonium-242 tracer: Dilute an NBS-certified (or equivalent) solution of plutonium-242 to a concentration of 10 dis min^{-1} ml^{-1} with 2M HNO_3 and store in glass.

6.7 Nitric acid, 2M: Add 125 ml of concd HNO_3 to 500 ml of water and dilute to 1 liter with water.

6.8 Nitric acid (HNO_3), 1M: Dilute 2M HNO_3 1:1 with water.

6.9 Sodium nitrite ($NaNO_2$), crystals.

6.10 Sodium nitrite solution, 3M: Dissolve 10.4 g of sodium nitrite ($NaNO_2$) in water and dilute to 50 ml with water. Make fresh daily.

6.11 Hydrochloric acid (HCl), 8M: Add 666 ml of concd HCl to 334 ml of water.

6.12 Thenoyltrifluoroacetone (TTA)-xylene solution, 0.5M TTA: Dissolve 111 g of $SC_4H_3COCH_2COCF_3$ (TTA) in xylene and dilute to 1 liter with xylene.

6.13 Ferric nitrate solution, 0.1M: Dissolve 40.4 g of ferric nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$] in water and dilute to 1 liter with water.

6.14 Hydroxylamine hydrochloride solution, 5M: Dissolve 347.5 g of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in water and dilute to 1 liter with water.

6.15 Hydrochloric acid — hydroxylamine hydrochloride solution, 0.5M HCl-0.05M $NH_2OH \cdot HCl$: Add 42 ml of concd HCl and 10 ml of 5M $NH_2OH \cdot HCl$ to 500 ml of water and dilute to 1 liter with water.

6.16 Praseodymium carrier solution: Dissolve 12.82 g of praseodymium nitrate dihydrate [$Pr(NO_3)_3 \cdot 2H_2O$] in 500 ml of water and dilute to 1 liter with water.

6.17 Anion exchange resin: Dowex 1-X4 (50-100 mesh, chloride form) or equivalent.

7. Procedure

7.1 Transfer a measured aliquot of the sample to an adequately sized beaker and adjust the acidity to 0.1M with concd HNO_3 if not previously adjusted.

7.2 Add 1 ml of 10 dis min^{-1} ml^{-1} plutonium-242 tracer solution.

7.3 Add 1.25 ml of 0.1M bismuth nitrate solution per liter of sample.

7.4 Add 1 g of $NaNO_2$ crystals per liter of sample.

7.5 Place on a hot plate and digest the sample solution at 70°C for 2 h with stirring.

7.6 Add 5.25 ml of concd H_3PO_4 per liter of sample, remove from heat, and stir frequently for 1 h.

7.7 Allow the $BiPO_4$ precipitate to settle overnight.

7.8 Without disturbing the precipitate, withdraw and discard the supernatant liquid.

7.9 Transfer the precipitate to a 100-ml glass centrifuge tube, centrifuge at 2000 rpm for 10 min, and discard the supernatant solution.

7.10 Transfer the precipitate to a 250-ml beaker with 25 ml of concd HNO_3 and heat to dissolve the precipitate.

7.11 Add an equal volume of water to adjust the acid to 8M.

7.12 Add 2 ml of 3M $NaNO_2$ solution and heat to boiling.

7.13 Allow the sample to digest for 20 min to adjust the valence of the plutonium to Pu^{+4}.

7.14 While the sample is digesting, prepare a resin column as follows.

7.14.1 Place a glass-wool plug in the bottom of the column as described in step 5.1.

7.14.2 Slurry the resin (see step 6.17) with water and immediately discard the fines by decanting. Repeat as necessary until fines are removed.

7.14.3 Transfer 4 ml of resin to the column with water. Prevent any channeling by maintaining the solution level above the resin using the stopcock.

7.14.4 Place a glass-wool plug on top of the resin.

7.14.5 Convert the resin to the nitrates form by passing several column volumes of 8M through the column until the resin is free of chloride ions.

7.15 Transfer the sample solution, which should be at room temperature, to the prepared resin column and allow it to flow through the column at a rate of 2 ml per minute. Discard the effluent solution.

7.16 Rinse the beaker with 25 ml of 8M HNO_3 and transfer the rinse to the column. Allow the 8M HNO_3 rinse to flow through the column at a rate of 2 ml per minute. Discard the effluent solution.

7.17 Rinse the beaker with 25 ml of 8M HCl and transfer the rinse to the column. Allow the 8M rinse to flow through the column at a rate of 2 ml per minute. Discard the effluent solution.

7.18 Add 1 drop of 0.1M $Fe(NO_3)_3$ and 1 ml of 5M $NH_2OH \cdot HCl$ to the column. Open the stopcock and allow the solution to drain to the top of the resin bed, then stop the flow. Discard the effluent solution.

7.19 Add 4 ml of 0.5M HCl-0.05M $NH_2OH \cdot HCl$ solution. Place a 50-ml glass centrifuge tube under the column. Allow 3 ml of solution to drain into the tube and close the stopcock.

7.20 Allow 20 min digestion time for reduction of the plutonium to Pu^{+3}.

7.21 Add 25 ml of 0.5M HCl-0.05M $NH_2OH \cdot HCl$ solution. Pass the solution through the column at a flow rate of 2 ml/min into the 50-ml tube.

7.22 Add 1 ml of praseodymium carrier to the sample solution in the 50-ml tube and mix thoroughly.

7.23 Add concd NH_4OH, with stirring, to a pH of 9. Allow 15 min digestion time.

7.24 Centrifuge for 10 min at 1500 rpm and discard the supernatant solution.

7.25 Wash the precipitate with water, centrifuge, and discard the water wash solution.

7.26 Dissolve the precipitate in 6 drops of concd HNO_3 and transfer the dissolved sample to a 50-ml extraction vial with 5 ml of 1M HNO_3. Add 10 drops of 3M $NaNO_2$, mix well, and allow 20 min digestion time for plutonium to oxidize to Pu^{+4}.

7.27 Add 1 ml of 0.5M TTA-xylene solution, and extract on a Vortex mixer for 10 min.

7.28 Centrifuge for 2 min to separate the phases. Discard the aqueous phase.

7.29 Scrub the TTA extract with 5 ml of 1M HNO_3. Centrifuge and discard the aqueous phase.

7.30 Transfer the TTA to a stainless steel disk placed on a hot plate set at 150°C. Allow the TTA to dry thoroughly.

7.31 Flame the stainless steel disk to a red heat.

7.32 Measure the alpha activities by pulsing with a silicon surface-barrier detector coupled to a multichannel analyzer.

8. Calculations

$$^{238}Pu = ACM/DE \quad , Bq/m^3 \ ,$$

$$^{239}Pu = BCM/DE \quad , Bq/m^3 \ ,$$

where

A = net integrated counts of ^{238}Pu from pulse analysis,

B = net integrated counts of ^{239}Pu from pulse analysis,

C = dis/min of ^{242}Pu added,

D = net integrated counts of ^{242}Pu from pulse analysis,

E = volume of sample, ml,

M = conversion factor from Bq; 1 Bq = 60 dis/min.

9. Precision and Accuracy

9.1 The precision is estimated to be ±20%. The accuracy has not been established.

Working Bibliography for Sect. 4.9

George H. Coleman, *The Radiochemistry of Plutonium*, National Academy of Sciences — National Research Council, NAS-NS 3058, September 1, 1965.

John J. Harley (ed.), *EML Procedures Manual*, HASL-300, 1972.

Frederick B. Johns (ed.), *Handbook of Radiochemical Analytical Methods*, EPA-680/4-75-001, February 1975.

4.10 The Determination of Transplutonium or Plutonium in Water Samples (performed by Bio-Assay Laboratory, Industrial Safety and Applied Health Physics Division)

1. Reagents

1.1 Nitric acid (HNO_3), concentrated

1.2 Phosphoric acid (H_3PO_4), concentrated

1.3 1M calcium nitrate [$Ca(NO_3)_2$]

1.4 Ammonium hydroxide (NH_4OH), concentrated

1.5 Hydroxylamine hydrochloride ($NH_2OH \cdot HCl$)

1.6 Phosphoric wash: 10 ml of concd H_3PO_4 with 1500 ml of distilled water. Add NaOH until a pH of 8 is obtained.

1.7 Dowex AG2-X8 (50-100 mesh, chloride form) anion resin

1.8 10M hydrochloric acid (HCl)

1.9 Hydriodic hydrochloric acid wash: Add 100 ml of 10M HCl to 0.5 ml of 47% hydriodic acid (HI).

1.10 5% sodium bisulfite ($NaHSO_3$)

1.11 4 to 6% sodium hypochlorite (NaOCl)

1.12 2M potassium hydroxide (KOH)

2. Special Equipment

2.1 Stainless steel disks, 1.27 cm diam

2.2 Electroplating cells, approximately 12.5-ml well

2.3 Platium electrodes

2.4 Power source capable of supplying at least + 10 V and 200 mA current

2.5 Alpha counting system

3. Procedure

3.1 Add 50 ml of concd HNO_3 to the 1-liter water sample.

3.2 Filter sample using Whatman No. 42 filter paper. Discard the paper after filtration.

3.3 Add 5 ml of concd H_3PO_4 and 4 ml of 1M $Ca(NO_3)_2$.

3.4 Heat sample to 85°C on a hot plate (with magnetic stirring).

3.5 Add 110 ml of concd NH_4OH and stir continuously for 1 h.

3.6 Use an evaporator dish as a cover for the water sample and allow to cool overnight.

3.7 Draw off as much of the supernatant as possible without disturbing the residue.

3.8 Discard the supernatant and transfer the residue to a centrifuge tube. Increase the volume to 100 ml with phosphoric wash.

3.9 Centrifuge for 5 min and discard supernatant.

3.10 Increase the volume to 100 ml and wash the residue.

3.11 Centrifuge for 5 min and discard the supernatant.

3.12 Add a minimum of hot concd HNO_3 to dissolve the residue. Transfer solution to a 100-ml beaker containing 80 to 90 ml of distilled water.

3.13 Evaporate to dryness.

3.14 Add 15 to 20 ml of 8M HNO_3 to the residue and evaporate to dryness. Dissolve the residue in 20 ml of 8M HNO_3.

3.15 Transfer sample to the anion exchange column, wash beaker with 10 ml of 8M HNO_3, and collect the transplutonium elutriant in a 100-ml beaker.

3.16 Wash the column with 30 ml of 8M HNO_3 and collect the wash in the 100-ml beaker containing the transplutonium elutriant.

3.17 Wash the column with 20 ml of 10M HCl and discard the wash.

3.18 Add 15 ml of hydriodic-hydrochloric acid to wash the column. Wash the column with 30 ml of 10M HCl. Collect the elutriant and all washing solutions in a 50-ml beaker.

3.19 Place the 50-ml beaker containing elutriant on a hot plate and evaporate to dryness.

3.20 Add four drops of concd HCl and 5 ml of distilled water to the residue.

3.21 Add 2 ml of 5% $NaHSO_3$ and evaporate to complete dryness on a hot plate.

3.22 Dissolve the residue in a minimum amount of distilled water.

3.23 Add 2 ml of 4 to 6% NaOCl and 5 ml of 2M KOH to the sample.

3.24 Place 1.27-cm-diam stainless steel disk in the bottom of a 12.5-ml well electroplating cell. Test the cell with distilled water for leakage overnight.

3.25 Discard distilled water before pouring samples into electroplated cells.

3.26 Evaporate the sample to 10 ml and transfer to the electroplating cell. Rinse the beaker well.

3.27 Place a platinum electrode into the sample-filled electroplating cell. Energize the electrode with a +10 V source and a current of 160 to 180 mA. Electroplate the disk for 5 h.

3.28 Remove the platinum wire from the cell and discard the solution.

3.29 Rinse the cell with distilled water and remove the electroplated disk. Use tweezers when removing the disk. Do not touch the face of the electroplate.

3.30 Dry the surface of the electroplated disk under a heat lamp. Flame the electroplated disk to a bright red by holding disk over a Bunsen burner.

3.31 Count the disk using the alpha counting technique for gross-alpha determination of either plutonium or transplutonium radionuclides, given below.

3.31.1 Special equipment for counting

a. Alpha scintillation counter with the permanent phosphor removed.

b. Silver-activated zinc sulfide [ZnS(Ag)] coated on Mylar disks 2.52 cm (15/16 in.) in diameter.

c. Nylon disk and ring assembly

3.31.2 Counting procedures. Label the nylon disk with date and location of sample. Place the electroplated transplutonium or plutonium sample inside the nylon disk and cover with a ZnS(Ag) Mylar disk. Place a phosphor disk on top of the ZnS(Ag) Mylar disk so that the phosphor side will be in direct contact with it. Place a nylon ring on top of the assembly and press firmly to ensure a snug fit. Cut away the excess Mylar.

Place the mounted sample in the alpha counter and count for 4 h. The background count is approximately 1 count/h with a counting efficiency of 50%.

$$\text{dis/min} = \frac{\text{counts/min - background counts/min}}{\text{0.5 efficiency}^*}$$

*The efficiency is measured as a percentage.

4.11 Radiochemical Method for Determining Thorium Isotopes in Water (performed by Analytical Chemistry Division Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

1.1 This method is applicable to the determination of the isotopes of thorium in potable, natural, and industrial waters.

1.2 The lowest concentration reported is 1.5×10^{-6} Bq/ml (4×10^{-5} pCi/ml) when analyzing a 1-liter sample, counting for 1000 min on an alpha pulse-height analyzer with a detector having a 20% efficiency and a 0.005-counts/min background over each energy region of interest, and realizing an 80% chemical recovery of the thorium.

2. Summary of Method

Thorium-234 tracer (a beta-gamma emitter) is equilibrated with the thorium isotopes in the sample. All of the thorium isotopes are coprecipitated with praseodymium as the hydroxide and the fluoride. The thorium is finally purified by extract and is dried on a stainless steel disk. The chemical yield is determined by evaluating the thorium-24 by beta counting and the alpha-emitting thorium isotopes are determined by alpha pulse-height analysis.

3. Sample Handling and Preservation

3.1 If suspended and/or soluble thorium determinations are desired, the samples should first be filtered to remove the suspended particulates as soon as practicable. The samples should then immediately be adjusted to a pH of 1 with nitric acid.

3.2 If total thorium determinations are desired, the samples should be adjusted to a pH of 1 as soon as practicable with filtering.

3.3 After pH adjustment, the samples are stored in glass or plastic container without filtering.

4. Interferences

This method does not separate uranium adequately when the uranium to thorium activity ratio is greater than 1. Several of the isotopes of uranium and thorium have alpha energies sufficiently close and will cause interferences in pulse-height analysis. Further purification procedures are recommended for thorium when the uranium concentration is known to be significant.

5. Apparatus

5.1 Vortex mixer
5.2 Hot plate
5.3 Centrifuge
5.4 Extraction vials, 50-ml with plastic-lined screw caps
5.5 Transfer pipettes
5.6 Beakers, size adequate to accommodate the sample aliquot
5.7 pH meter with combination electrode.
5.8 Stainless steel disk, sized to be compatible with counting systems.
5.9 Multichannel analyzer system with silicon surface-barrier detector(s)
5.10 Beta counter, adequate to accommodate the stainless steel disks
5.11 Plastic centrifuge tubes, 50-ml and 100-ml
5.12 Water bath

6. Reagents

6.1 Praseodymium solution, 5 mg/ml. Dissolve 6.00 g $Pr(NO_3)_3 \cdot 6H_2O$ in dilute HNO_3 and dilute to 500 ml with water.
6.2 Ammonium hydroxide (NH_4OH), concentrated
6.3 Potassium dichromate ($K_2Cr_2O_7$), 0.4M. Dissolve 11.8 g $K_2Cr_2O_7$ in water and dilute to 100 ml.
6.4 Hydrofluoric acid (HF), concentrated
6.5 Aluminium nitrate solution, 2M. Dissolve 75.0 g $Al(NO_3)_3 \cdot 9H_2O$ in water and dilute to 100 ml.
6.6 Nitric acid (HNO_3), concentrated

6.7 Nitric acid (HNO_3), 1M. Dilute 6.25 ml concd HNO_3 to 100 ml with water.

6.8 HNO_3 solution, pH 1.5. Transfer 500 ml of water to an 800-ml beaker. Immerse the pH electrode, stir, and adjust the pH to 1.5 with cond HNO_3.

6.9 TTA-xylene solution, 0.5M TTA. Dissolve 55.5 g TTA (thenoyltrifluoroacetone) in xylene and dilute to 500 ml with xylene.

6.10 Thorium tracer, thorium-234. Dissolve 1 g of U_3O_8 in dilute HNO_3 and convert to the chloride. Dissolve uranium chloride in 8M HCl and extract uranium with 20% (w/v) Adogen 364 in xylene. Retain the aqueous phase for the thorium tracer. Count for thorium-234 activity.

6.11 Ammonium hydroxide (NH_4OH), dilute. Transfer 35 ml concd NH_4OH to a 500-ml flask. Dilute to volume with water.

6.12 Hydrofluoric acid-nitric acid solution, 1M HF-1M-HNO_3. Mark a polyethlene bottle at the 100-ml volume level. Add 75 ml of water to the bottle. Using a plastic pipette, add 4 ml concd HF. Then add 6.25 ml concd HNO_3. Dilute to the 100-ml mark with water.

7. Procedure

7.1 Transfer a measured aliquot of the sample to an adequately sized beaker; check the pH and, if necessary, add HNO_3 to adjust the pH to 1.

7.2 Add 5,000 to 10,000 counts/min of thorium-234 tracer and 1 ml of praseodymium solution.

7.3 Place the beaker on a hot plate and allow the sample to heat to near boiling.

7.4 Remove the sample from the hot plate and allow to cool.

7.5 Add concd NH_4OH with stirring to a pH of 9.

7.6 Stir the sample frequently and allow the precipitate to settle (preferably overnight).

7.7 Decant the supernatant solution and transfer the precipitate to a 50- or 100-ml centrifuge tube.

7.8 Centrifuge at 2000 rpm for about 10 min.

7.9 Discard the supernatant solution.

7.10 Wash the precipitate with water, centrifuge, and discard the water wash solution.

7.11 Dissolve the precipitate with 8 to 10 drops of concd HNO_3.

7.12 Add approximately 0.3 ml of 0.4M $K_2Cr_2O_7$.

7.13 Digest in a hot water bath that is near the boiling point for 10 min.

7.14 Remove from the bath and add approximately 0.3 ml of concd HF. Mix well and allow to digest at room temperature for 10 min.

7.15 Centrifuge at 2000 rpm for 5 min.

7.16 Add 2 drops of praseodymium solution and swirl gently without disturbing the precipitate.

7.17 Repeat step 7.15.

7.18 Discard the supernatant solution.

7.19 Wash the precipitate with approximately 2 ml of 1M HF-1M HNO_3 solution that contains 3 drops of 0.4M $K_2Cr_2O_7$.

7.20 Repeat steps 7.15 and 7.18.

7.21 Dissolve the fluoride precipitate with 0.5 ml of 2M $Al(NO_3)_3$ and 5 drops of 1M HNO_3.

7.22 Transfer the solution to a 50-ml vial.

7.23 Rinse the tube with 5 ml of distilled water and add the rinse solution to the 50-ml vial.

7.24 With the aid of the pH meter, adjust the pH of the solution from 1.4 to 1.5 with dilute NH_4OH and/or dilute HNO_3.

7.25 Add 2 ml of 0.5M TTA-xylene.

7.26 Mix on the Vortex mixer for 10 min.

7.27 Centrifuge at 2000 rpm for about 5 min.

7.28 Transfer the TTA to a new vial.

7.29 Repeat steps 7.25 through 7.28, transferring the second TTA to the same vial.

7.30 Scrub the TTA with 5 ml of pH 1.5 HNO_3 solution.

7.31 Repeat step 7.27 and discard the scrub solution.

7.32 Evaporate the entire TTA extract on a stainless steel disk and flame the disk to red.

7.33 Count the sample disk and a thorium-234 comparator disk on a beta counter. Ratio the sample net count to the comparator net count to determine the fraction of thorium recovery.

7.34 Perform an alpha pulse-height analysis to determine the identity and quantity of the thorium isotopes present in the sample.

8. Calculations

Thorium-x, Bq/ml = ABM/DV

where

A = the net integrated counts (counts/min) of thorium-x from the pulse-height analysis,

B = the efficiency factor of the alpha pulse-height analyzer system,

D = the fraction of ^{234}Th recovered,

V = the volume of the sample, ml,

x = isotope of interest.

M = conversion factor to Bq; 1 Bq = 60 dis/min.

9. Precision and Accuracy

9.1 The precision is estimated to be 20% at the 95% confidence level.

9.2 The accuracy of this method has not been established; however, repeated determinations on solutions of known concentrations do not indicate significant bias.

Working Bibliography for Sect. 4.11

F. L. Moore, "Radiochemical Determination of Ionium in Uranium Fluorination Ash," *Analytical Chemistry* 30, 1020, (1958).

4.12 Sampling for the National Pollutant Discharge Elimination System (NPDES)

1. Weekly, a technician collects water samples from Melton Branch (MB), White Oak Creek (WOC), and the Sewage Treatment Plant (STP). Approximately 1000 ml of water per analysis is collected and delivered to the Environmental Analysis Laboratory (Product Certification Division, Y-12) and the Analytical Chemistry Section (Technical Service Division, K-25). For information concerning these analyses, refer to the Summary Chart.

2. The dissolved oxygen (DO), pH, and flow are read and recorded on-site daily at WOC and MB, while the chlorine and pH values are read and recorded for the STP. To take accurate readings, the tests are conducted as presented here and the sample is thoroughly mixed before each test. After collecting the sample, the DO probe is connected to the Dor-4A-Montedoro Meter (manufactured by the Whitney Corporation), and the battery is checked. If a value of 9 is displayed on the meter, the power is sufficient to take the DO reading. The meter switch is changed to DO, and the probe is rinsed with distilled water. The probe is inserted into the sample, and the value is recorded. The probe is disconnected from the meter, rinsed with distilled water, and stored in a moist container. Add distilled water to the container if it is not moist.

3. The pH reading is taken after the reading of the DO value at WOC and MB and after the chlorine reading at STP. The pH meter is calibrated to 7.0 with a neutral buffer. The electrode is rinsed with distilled water, immersed into the sample, and the value of the sample is read from the Digi-Sense pH Meter (manufactured by the Cole Palmer Instrument Corporation). The electrode is rinsed and its cap is filled with distilled water (to help keep the electrode moist) while in storage.

4. The Ecolab Test Kit for DPD chlorine (manufactured by Ecologic Instrument Corporation) is used to determine the free chlorine level at the STP. The sample tube is rinsed with the water sample. Ten drops of Reagent 1 and 6 drops of Reagent 2 are added to the tube. The tube is filled with sample water and thoroughly mixed. Six drops of Reagent 3 are added to the sample and thoroughly mixed. The tube is placed in the Chlorine Comparator DPD, and the corresponding value is recorded.

5. A summary of all analyses conducted on samples collected for the NPDES is presented in the Summary Chart. The laboratory procedures for these analyses are presented in this section.

6. The routing procedures below only include the present NPDES monitoring sites and are subject to revision when a new NPDES permit is issued.

   From the 4500-South parking lot, drive east 0.16 km (0.1 mile) and turn right onto Southside Drive. Travel west 0.48 km (0.3 mile) and turn left onto White Oak Avenue. Proceed 0.32 km (0.2 mile) to the entrance of the Sewage Treatment Plan (STP). The STP entrance is directly across from Building 2523 and to the left of the Tool Store. Drive to the STP control building and park. The effluent site (003) is located behind the control building at the furthermost part of the chlorine basin. The influent monitoring site (003) is located in front of the control building (2521) at the point where the pipe feeds wastewater into the treatment basin.

   Return to White Oak Avenue and turn left. Travel approximately 0.02 km (50 ft) to the West Portal and turn left onto First Street. Proceed on First Street (Lagoon Road) for approximately 1.29 km (0.8 mile) to the Chemical Waste Area Access Road (CWAA). Turn left onto CWAA road and proceed approximately 1.29 km (0.8 mile) to White Oak Creek (WOC) sampling station (001). Continue on CWAA Road for 0.1 mile veering to the right at the Y-intersection. Melton Branch monitoring site (002) is located on the left.

Return to Lagoon Road and turn right. Drive 0.8 miles to the West Portal and turn left. Travel on White Oak Avenue for approximately 0.32 km (0.2 mile) and turn right onto South Side Drive. Proceed 0.48 km (0.3 mile) to White Oak Avenue. Turn left and travel approximately 0.14 km (450 ft) to the 4500-South parking lot.

4.13 Analytical Procedures for the Determination of Total Metals in Water Atomic Absorption Method

(performed by Analytical Chemistry Division Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

Metals in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in drinking, surface, and saline waters, and in domestic and industrial wastes. While drinking water may be analyzed directly, domestic and industrial wastes require processing to solubilize suspended material.

2. Summary of Method

In atomic absorption spectrophotometry, a light beam is directed through a flame into a monochromator and onto a detector. A sample is atomized and aspirated into the flame where absorption takes place. Because the wavelength of the light beam is a characteristic of the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample.

3. Sample Handling and Preservation

For the determination of total metals, the sample is acidified with 1:1 HNO_3 to a pH of 2 at the time of collection. The sample is not filtered before processing.

4. Interferences

4.1 The presence of many dissolved solids in the sample may result in an interference from nonatomic absorbance such as light scatter. If background correction is not available, a nonabsorbing wavelength should be checked.

4.2 Ionization interferences occur when the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positively charged ion. This type of interference can be controlled by adding an excess of an easily ionized element to standards and samples.

5. Apparatus

5.1 Atomic absorption spectrophotometer. Any commercial atomic absorption instrument having an energy source, an atomizer burner system, a monochromator, and a detector is suitable.

5.2 Burner. The burner recommended by the instrument manufacturer should be used.

5.3 Glassware. All glassware, including sample bottles, should be washed with detergent and rinsed with tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water, and deionized (distilled) water, in that order.

6. Reagents

6.1 Deionized water

6.2 Nitric acid (HNO_3), concentrated. Use a "high purity" grade acid if metal impurities are found in reagent grade acid. Prepare a 1:1 dilution with deionized water.

6.3 Hydrochloric acid (HCl), 1:1. Prepare a 1:1 dilution of reagent grade acid with deionized water. If metal impurities are found to be present, use a "high purity" grade acid.

6.4 Ionization suppressant. Dissolve 129.28 g of potassium nitrate (KNO_3) in deionized water and dilute to 1 liter. This solution contains 50,000 µg/ml potassium. Samples and standards to be analyzed for easily ionized metals should contain 2000 µg/ml potassium to suppress ionization.

7. Preparation of Standards and Calibration

7.1 Stock solutions are prepared from high purity metals, oxides, or nonhygroscopic reagent grade salts using nitric or hydrochloric acids of suitable purity. The stock solutions

are prepared at concentrations of 1000 µg of the metal per liter. Commercially available stock standard solutions may also be used.

7.2 Standard solutions are prepared by diluting the stock metal solutions. Prepare a blank and calibration standards in graduated amounts in the appropriate range for each metal. The calibration standards should be prepared using the same type of acid and at the same concentration as in the samples after processing. Beginning with the blank and working toward the highest standard, aspirate the solutions and record the readings. Repeat the operation with both the standards and the samples a sufficient number of times to secure a reliable average reading for each sample.

7.3 Where the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard additions must be used.

8. Procedure

8.1 Transfer a representative aliquot of the well-mixed sample to a covered beaker and add 3 ml of concd HNO_3.

8.2 Place the beaker on a hot plate and evaporate to dryness cautiously, making certain that the sample does not boil.

8.3 Cool the beaker and add another 3-ml portion of concd HNO_3.

8.4 Return the beaker to the hot plate and increase the temperature so that a gentle reflux action occurs.

8.5 Continue heating, adding additional acid as necessary, until the digestion is complete – generally indicated by a light-colored residue.

8.7 Wash down the beaker walls and watch glass with deionized water.

8.8 Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis.

Note:

The analysis of silver requires modification of the digestion procedure to exclude HCl.

9. Calculation

9.1 mg/liter metal in sample = $\frac{AB}{C}$

where:

A = mg/liter of metal in processed sample,
B = final volume of processed sample, ml,
C = volume of sample aliquot processed, ml.

Concentrations so determined shall be reported as "total."

9.2 Table 4.13-1 shows the lowest concentration reported (LCR) for each metal:

Table 4.13-1. Lowest concentration reported for various metals

Element	Concentration (mg/liter)
Ag	0.01
Al	0.05
Ba	0.2
Ca	0.1
Cd	0.002
Cr	0.01
Cu	0.004
Fe	0.06
K	0.1
Li	0.01
Mg	0.1
Mn	0.01
Mo	0.1
Na	0.1
Ni	0.01
Pb	0.01
Zn	0.02

10. Precision and Accuracy

10.1 The precision and accuracy of this technique have not been established.

Working Bibliography for Sect. 4.13

Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, p. 78, (1976).

4.14 Colorimetric Determination of Phenols in Water

(performed by Analytical Chemistry Division Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Introduction

Steam-distillable phenols react with 4-aminoantipyrine at a pH of 10.0 ± 0.2 in the presence of potassium ferricyanide to form a colored antipyrine dye. This dye is extracted from aqueous solution with chloroform and the absorbance is measured at 450 nm.

2. Reagents

2.1 4-Aminoantipyrine
2.2 Ammonium chloride (NH_4Cl)
2.3 Ammonium hydroxide
2.4 Chloroform
2.5 Phenol
2.6 Potassium ferricyanide
2.7 Sodium sulfate

3. Equipment

3.1 Beakers, 600-ml
3.2 Distillation apparatus
3.3 Pipettes, 5-ml, 10-ml, 15-ml, 20-ml, and 25-ml
3.4 Separatory funnels, 1000-ml, with Teflon stopcocks
3.5 Spectrophotometer, DK-2A, with 10-cm cells

4. Preparation of Standard Solutions

4.1 Ammonium chloride (NH_4Cl). Dissolve 50 g of NH_4Cl in distilled water and dilute to 1000 ml.
4.2 Aminoantipyrine solution. Dissolve 0.50 g of 4-aminoantipyrine in distilled water and dilute to 100 ml. Prepare fresh for each day of use.

4.3 Potassium ferricyanide [$K_3Fe(CN)_3$] solution. Dissolve 2.0 g of $K_3Fe(CN)_3$ in distilled water and dilute to 100 ml. Prepare fresh for each week of use.

4.4 Stock phenol (C_6H_5OH) solution, 1000 mg/liter. Dissolve 1.00 g of reagent-grade phenol in freshly boiled and cooled distilled water and dilute to 1000 ml.

4.5 Standard phenol (C_6H_5OH) solution, 0.5 mg/liter. Dilute 0.050 ml of the stock phenol solution to 100 ml with freshly boiled and cooled distilled water. Use immediately.

5. Determination of Calibration Curve

5.1 Prepare seven 600-ml beakers and add standard phenol solution as shown in Table 4.14-2 and dilute to 500-ml mark with distilled water.

Table 4.14-2. Phenol calibration

Standard No.	Standard phenol solution (ml)	Final volume (ml)	Phenol concentration (mg/liter)
1	0	500	0
2	0	500	0
3	5	500	0.005
4	10	500	0.010
5	15	500	0.015
6	20	500	0.020
7	25	500	0.025

5.2 Treat standards as samples beginning with step 6.3.

5.3 Plot absorbance versus concentration of phenol in milligrams per liter.

6. Procedures

6.1 Measure 500 ml of the preserved sample into a 1-liter distilling flask and connect the condenser to the flask.

6.2 Distill 450 ml of sample; stop the distillation and, when boiling ceases, add 50 ml of distilled water to the flask. Resume the distillation until a total of 500 ml has been collected in a 600-ml beaker.

6.3 Add 10 ml of NH_4Cl solution and adjust the pH to 10.0 ± 0.2 with concd NH_4OH.

6.4 Transfer to a 1-liter separatory funnel; add 5.0 ml of aminoantipyrine solution; mix well and add 5.0 ml of potassium ferricyanide solution; mix well again and allow the color to develop for 3 min.

6.5 Pipette 40 ml of chloroform into each funnel and shake 10 times, allow the chloroform to settle, shake again 10 times, and allow phases to separate.

6.6 Drain the chloroform layer into a beaker that contains ∿0.25 g of sodium sulfate. Combine both blank extracts.

6.7 Measure the absorbance at 450 nm against the reagent blank.

7. Calculations

mg phenols/liter = (Abs x Factor)

Concentration of phenols in milligrams per liter is read from the previously prepared standard calibration curve. The lowest concentration of phenols that should be reported is 0.001 mg/liter.

4.15 Analytical Procedures for Settleable Solids, Volumetric Method

(performed by Environmental Analysis Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

This method is applicable to surface and saline waters, domestic and industrial wastes.

2. Summary of Method

2.1 Settleable matter is measured volumetrically with an Imhoff cone.

2.2 Based on a settling time of 1 h, the lowest concentration reported is 0.1 ml/liter.

3. Apparatus and Reagents

3.1 The only apparatus required is an Imhoff cone.

3.2 No reagents are required.

4. Procedure

4.1 By volume

4.1.1 Fill an Imhoff cone to the 1-liter mark with a thoroughly mixed sample.

4.1.2 Let sample settle for 45 min.

4.1.3 Gently stir the sides of the cone with a rod or by spinning.

4.1.4 Let sample settle for an additional 15 min.

4.1.5 Record volume of settleable matter in the cone as milliliters per liter. Disregard any floating materials that may be present; they are not to be counted in the volume of settleable matter.

5. Calculation

5.1 The milliliters per liter of settleable matter is the recorded volume of settleable matter in the cone.

6. Precision and Accuracy

No data are available at this time.

Working Bibliography for Sect. 4.15

Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 916, Method No. 208F (1975).

4.16 Analytical Procedures for Total Solids, Gravimetric Method (performed by Environmental Analysis Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

   1.1 This method is applicable to drinking, surface, and saline waters and to domestic and industrial wastes.

   1.2 The range of the method is dependent upon sample size.

2. Summary of Method

   2.1 Total solids are the sum of homogeneous suspended and dissolved materials in a sample. A well-mixed aliquot of the test sample is quantitatively transferred to a preweighed evaporating dish and evaporated to dryness at 103 to 105°C. The weight of the dried residue is a measure of the total solids in the sample.

   2.2 When a 100-ml sample is analyzed, the lowest concentration reported is 5 mg/liter.

3. Sample Handling and Preservation

   Sample preservation is not practical; analyze as soon as possible.

4. Interferences

   4.1 Large floating particles or submerged agglomerates (nonhomogeneous materials) should be excluded from the test sample.

   4.2 Floating oil and grease, if present, should be included in the sample and dispersed by a blender device before aliquoting.

5. Apparatus

   5.1 Porcelain evaporating dishes, 90-mm, 100-ml capacity. (Vycor or platinum dishes may be substituted).

   5.2 Blender, any commercial type.

6. Procedure

   6.1 Heat the clean evaporating dish to 550 ± 50°C for 1 h in a muffle furnace. Cool, desiccate, weigh, and store in desiccator until ready for use.

6.2 Transfer a measured aliquot of sample to the preweighed dish and evaporate to dryness on a steam bath or in a drying oven.

6.2.1 Choose an aliquot of sample sufficient to contain a residue of at least 25 mg. To obtain a weighable residue, successive aliquots of sample may be added to the same dish.

6.2.2 If evaporation is performed in a drying oven, the temperature should be lowered to approximately 98°C to prevent boiling and spattering of the sample.

6.3 Dry the evaporated sample for at least 1 h at 103 to 105°C. Cool in a desiccator and weigh. Repeat the cycle of drying at 103 to 105°C, cooling, desiccating, and weighing until a constant weight is obtained or until loss of weight is less than 4% of the previous weight or 0.5 mg, whichever is less.

7. Calculation

Calculate total solids as follows:

$$\text{Total solids} = \frac{(A - B) \times 1000 \text{ ml/liter}}{C}, \quad \text{mg/liter},$$

where

A = weight of sample + dish, mg,
B = weight of dish, mg,
C = volume of sample, ml.

Working Bibliography for Sect. 4.16

Manual of Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, p. 270 (1976).

Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 91, Method 208A (1975).

4.17 Analytical Procedures for Undissolved Solids, Gravimetric Method (performed by Environmental Analysis Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

   1.1 This method is applicable to drinking, surface, and saline waters, and to domestic and industrial wastes.

   1.2 The range of the method is dependent upon sample size. The lowest concentration reported is 5 mg/liter when a 100 ml sample is analyzed.

2. Summary of Method

   2.1 A well-mixed sample is filtered through a standard glass-fiber filter, and the solids retained on the filter are dried to constant weight at 103 to 105°C.

   2.2 The filtrate from this method may be used for determining dissolved solids as presented in Analytical Procedures for Dissolved Solids, Gravimetric Method (Procedure 4.19).

3. Sample Handling and Preservation

   3.1 Nonhomogeneous particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample.

   3.2 Preservation of the sample is not practical; analysis should begin as soon as possible.

4. Interferences

   Too much residue on the filter will trap water and prolong drying.

5. Apparatus

   5.1 Glass-fiber filter disks, 4.25-cm or 2.1-cm, without organic binder, Reeve Angel type 934 AH, or equivalent

   5.2 Filter holder, membrane filter funnel or Gooch crucible adapter

   5.3 Suction flask, 500-ml

5.4 Gooch crucibles, 25-ml (if 2.1-cm filter is used)

5.5 Drying oven, 103 to 105°C

5.6 Desiccator

5.7 Analytical balance, 200-g capacity, capable of weighing to 0.1 mg

6. Procedure

6.1 Preparation of glass-fiber filter disk: Place the disk on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible. While vacuum is applied, wash the disk with three successive 20-ml volumes of distilled water.

Remove all traces of water by continuing to apply vacuum after water has passed through. Remove filter from membrane filter apparatus (or both crucible and filter if Gooch crucible is used), and dry in an oven at 103 to 105°C for 1 h. Place in desiccator and store until needed. Weigh immediately before use.

6.2 Assemble the filtering apparatus and apply suction. Shake the sample vigorously and rapidly transfer 100 ml to the funnel by means of a 100-ml graduated cylinder. Larger volumes can be analyzed if the suspended matter is low.

6.3 Carefully remove the filter from the membrane filter funnel assembly. Alternatively, remove crucible and filter from crucible adapter. Dry at least 1 h at 103 to 105°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained or until weight loss is less than 0.5 mg.

7. Calculations

Calculate undissolved solids as follows:

$$\text{Undissolved solids, mg/liter} = \frac{(A - B) \times 1000 \text{ ml/liter}}{C},$$

where

A = weight of filter + residue, mg,

B = weight of filter, mg,

C = ml of sample filtered.

8. Precision and Accuracy

No data are available at this time.

Working Bibliography for Sect. 4.17

Manual of Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, p. 268 (1976).

4.18 Analytical Procedures for Determining Turbidity (performed by Environmental Analysis Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

This method is applicable to drinking, surface, and saline waters in the range of turbidity from 0 to 40 nephelometric turbidity units (NTU). NTUs are considered comparable to the previously reported Formazin Turbidity Units (FTU) and Jackson Turbidity Units (JTU).

2. Summary of Method

2.1 The method is based upon a comparison of the intensity of light scattered by the sample under defined conditions, with the intensity of light scattered by a standard reference suspension. The higher the intensity of scattered light, the higher the turbidity. Readings, in NTUs, are made in a nephelometer designed according to specifications outlined in step 5. A standard suspension of Formazin, prepared under closely defined conditions, is used to calibrate the instrument. Formazin polymer is used as the turbidity reference suspension for water because it is more reproducible than other types of standards previously used for turbidity standards.

2.2 The lowest turbidity reported is 0.05 NTU (1.1).

3. Sample Handling and Preservation

Samples taken for turbidity measurements should be analyzed as soon as possible. Preservation of samples is not recommended.

4. Interferences

4.1 The presence of floating debris and coarse sediments which settle out rapidly will give low readings. Finely divided air bubbles will give readings higher than normal.

4.2 The presence of true color, that is, a color of water caused by dissolved substances which absorb light, will cause turbidities to be low. This effect is generally not significant with finished waters.

5. Apparatus

5.1 The turbidimeter shall consist of a nephelometer with light source for illuminating the sample and one or more photoelectric detectors with a readout device to indicate the intensity of light scattered at right angles to the path of the incident light. The turbidimeter should be so designed that little stray light reaches the detector in the absence of turbidity and should be free from significant drift after a short warm-up period.

5.2 The sensitivity of the instrument should permit detection of turbidity differences of 0.02 unit or less in waters having turbidities less than 1 unit. The instrument should measure from 0 to 40 units of turbidity. Several ranges will be necessary to obtain both adequate coverage and sufficient sensitivity for low turbidities.

5.3 The sample tubes to be used with the available instrument must be of clear, colorless glass. They should be kept scrupulously clean, both inside and out, and discarded when they become scratched or etched. They must not be handled at all where the light strikes them, but should be provided with sufficient extra length or with a protective case for handling.

5.4 Differences in physical design of turbidimeters will cause differences in measured values for turbidity even though the same suspension is used for calibration. To minimize such differences, the following design criteria should be observed.

5.4.1 Light source: Tungsten lamp operated at not less than 85% of rated voltage or more than rated voltage.

5.4.2 Total distance traversed by incident light and scattered light within the sample tube must not exceed 10 cm.

5.4.3 Angle of light acceptance of the detector must be centered at 90° to the incident light path and must not exceed ±30° from 90°.

5.4.4 Maximum turbidity to be measured: 40 units.

5.5 The Hach Turbidimeter, Model 2100 or 2100 A, is in wide use and has been found to be reliable; however, other instruments meeting the above design criteria are acceptable.

6. Reagents

6.1 Turbidity-free water: Pass distilled water through a 0.45-μ pore-size membrane filter if such filtered water shows a lower turbidity than the distilled water.

6.2 Stock turbidity suspension:

Solution 1: Dissolve 1.00 g hydrazine sulfate, $[(NH_2)_2 \cdot H_2SO_4]$ in distilled water and dilute to 100 ml in a volumetric flask.

Solution 2: Dissolve 10.00 g hexamethylenetetramine in distilled water and dilute to 100 ml in a volumetric flask.

In a 100-ml volumetric flask, mix 5.0 ml of solution 1 with 5.0 ml of solution 2. Allow to stand 24 h at 25 ± 3°C, then dilute to the mark and mix.

6.3 Standard turbidity suspension: Dilute 10.00 ml of stock turbidity suspension to 100 ml with turbidity-free water. The turbidity of this suspension is defined as 40 units. Dilute portions of the standard turbidity suspension with turbidity-free water as required.

A new stock turbidity suspension should be prepared each month. The standard turbidity suspension and dilute turbidity standards should be prepared weekly by dilution of the stock turbidity suspension.

7. Procedure

7.1 Turbidimeter calibration: The manufacturer's operating instructions should be followed. Measure standards on the turbidimeter

covering the range of interest. If the instrument is already calibrated in standard turbidity units, this procedure will check the accuracy of the calibration scales. At least one standard should be run in each instrument range to be used. Some instruments permit adjustments of sensitivity so that scale values will correspond to turbidities. Reliance on a manufacturer's solid scattering standard for setting overall instrument sensitivity for all ranges is not acceptable practice unless the turbidimeter has been shown to be free of drift on all ranges. If a precalibrated scale is not supplied, then calibration curves should be prepared for each range of the instrument.

7.2 Turbidities less than 40 units: Shake the sample to disperse the solids thoroughly. Wait until air bubbles disappear, then pour the sample into the turbidimeter tube. Read the turbidity directly from the instrument scale or from the appropriate calibration curve.

7.3 Turbidities exceeding 40 units: Dilute the sample with one or more volumes of turbidity-free water until the turbidity falls below 40 units. The turbidity of the original sample is then computed from the turbidity of the diluted sample and the dilution factor. For example, if 5 volumes of turbidity-free water were added to 1 volume of sample and the diluted sample showed a turbidity of 30 units, then the turbidity of the original sample was 180 units.

The Hach Turbidimeters, Models 2100 and 2100A, are equipped with five separate scales: 0 to 0.2, 0 to 1.0, 0 to 100, and 0 to 1000 NTU. The upper scales are to be used only as indicators of required dilution volumes to reduce readings to less than 40 NTU.

8. Calculation

8.1 Multiply sample readings by appropriate dilution to obtain final reading.

$$NTU = RD$$

where

R = reading,

D = dilution factor.

8.2 Report results as follows:

NTU	Record to nearest
0.0-1.0	0.05
1-10	0.1
10-40	1
40-100	5
100-400	10
400-1000	50
>1000	100

9. Precision and Accuracy

9.1 In an Environmental Protection Agency laboratory using surface water samples at levels of 26, 41, 75, and 180 NTU, the standard deviations were ±0.60, ±0.94, ±1.2, and ±4.7 units respectively.

9.2 Accurate data are not available at this time.

Working Bibliography for Sect. 4.18

Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, p. 295 (1976).

Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 132, Method No. 2121A (1975).

4.19 Analytical Procedures for Dissolved Solids, Gravimetric Method (performed by Environmental Analysis Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

   1.1 This method is applicable to drinking, surface, and saline waters, and domestic and industrial wastes.

   1.2 The range of the method is dependent upon sample size. The lowest concentration reported is 5 mg/liter.

2. Summary of Method

   2.1 A well-mixed sample is filtered through a standard glass fiber filter. The filtrate is evaporated and dried to constant weight at 180°C. The weight of the dried residue is a measure of the dissolved solids in the sample.

   2.2 If undissolved solids (see Sect. 4.17) are being determined, the filtrate from that method may be used for determining dissolved solids.

3. Sample Handling and Preservation

   3.1 Preservation of the sample is not practical; analysis should begin as soon as possible.

4. Interferences

   4.1 Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and will require prolonged drying, desiccation, and rapid weighing.

   4.2 Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 103°C to ensure that all the bicarbonate is converted to carbonate.

   4.3 Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue should be limited to about 200 mg.

5. Apparatus

5.1 Glass fiber filter disks, 4.25 cm or 2.1 cm, without organic binder, Reeve Angle type 934 AH or equivalent

5.2 Filter holder, membrane filter funnel, or Gooch crucible adapter

5.3 Suction flask, 500-ml

5.4 Gooch crucibles, 25-ml (if 2.1-cm filter is used)

5.5 Evaporating dishes, porcelain, 200-ml volume. (Vycor or platinum dishes may be substituted.)

5.6 Steam bath

5.7 Drying oven, 103°C ± 2°C

5.8 Desiccator

5.9 Analytical balance, 200-g capacity, capable of weighing to 0.1 mg

5.10 Muffle furnace

6. Procedure

6.1 Preparation of glass fiber filter disk: Place the disk on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible. While vacuum is applied, wash the disk with three successive 20-ml volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Discard washings.

6.2 Preparation of evaporating dishes: Heat the clean dish to 550 ± 50°C for 1 h in a muffle furnace. Cool in desiccator and store until needed. Weigh immediately before use.

6.3 Assemble the filtering apparatus and begin suction. Shake the sample vigorously and rapidly transfer 100 ml to the funnel using a 100-ml graduated cylinder. If total dissolved solids is low, a larger volume may be filtered.

6.4 Filter the sample through the glass fiber filter and continue to apply vacuum for about 3 min after filtration is complete to remove as much water as possible.

6.5 Transfer 100 ml (or a larger volume) of the filtrate to a weighed evaporating dish and evaporate to dryness in a steam bath.

6.6 Dry the evaporated sample for at least 1 h at 103°C ± 2°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained or until weight loss is less than 0.5 mg.

7. Calculation

Calculate dissolved solids as follows:

$$\text{Dissolved solids, mg/liter} = \frac{(A - B) \times 1000 \text{ ml/liter}}{C}$$

where

A = weight of dried solids + dish, mg

B = weight of dish, mg

C = volume of filtrate used, ml.

Working Bibliography for Sect. 4.19

Manual of Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, p. 266, 1976.

4.20 Analytical Procedures for Total Oil and Grease, Gravimetric Method (performed by Environmental Analysis Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

1.1 This method includes the measurement of Freon-113-extractable matter from surface and saline waters and from industrial and domestic wastes. It is applicable to the determination of relatively nonvolatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and related matter.

1.2 Some crude oils and heavy fuel oils contain a significant percentage of residue-type materials that are not soluble in Freon-113. Accordingly, recoveries of these materials will be low.

1.3 The method is not applicable to the measurement of light hydrocarbons that volatilize at temperatures below 70°C. Petroleum fuels from gasoline through No. 2 fuel oils are completely or substantially lost in the solvent removal operation.

2. Summary of Method

2.1 The sample is acidified to a low pH (<2) and serially extracted with Freon-113 in a separatory funnel. The solvent is evaporated from the extract and the residue weighed.

2.2 When a 1-liter sample is analyzed, the lowest concentration reported is 2 mg/liter.

2.3 The definition of grease and oil is based on the procedure used. The source of the oil and/or grease and the presence of extractable nonoily matter will influence the material measured and interpretation of results.

3. Sample Handling and Preservation

3.1 A representative sample of 1-liter volume should be collected in a glass bottle. If analysis is to be delayed for more than a few hours, the sample is preserved by the addition of 5 ml of H_2SO_4 or HCl (see step 5.1) at the time of collection.

3.2 Because losses of grease will occur on sampling equipment, the collection of composite samples is impractical. Individual portions collected at prescribed time intervals must be analyzed separately to obtain the average concentration over an extended period.

4. Apparatus

4.1 Separatory funnel, 2000-ml, with Teflon stopcock

4.2 Vacuum pump or other source of vacuum

4.3 Flask, distilling, 125-ml

4.4 Filter paper, Whatman No. 40, 11-cm

5. Reagents

5.1 Sulfuric acid (H_2SO_4), 1:1. Mix equal volumes of concd H_2SO_4 and distilled water. (Concentrated hydrochloric acid may be substituted directly for concentrated H_2SO_4 for this reagent.)

5.2 Freon-113 (bp 48°C), 1,1,2-trichloro-1,2,2-trifluoroethane. At this time, reagent-grade Freon-113 is not available commercially. Freon-113 is available from E. I. DuPont de Nemours, Inc., and its distributors in 5-gal cans. It is best handled by filtering 1-gal quantities through paper into glass containers and by maintaining a regular program of solvent blank monitoring.

5.3 Sodium sulfate (Na_2SO_4), anhydrous crystal

6. Procedure

6.1 Mark the sample bottle at the water meniscus for later determination of sample volume. If the sample was not acidified at time of collection, add 5 ml H_2SO_4 or HCl reagent (see step 5.1) to the sample bottle. After mixing the sample and reagent, check the pH by touching pH-sensitive paper to the cap to ensure that the pH is 2 or lower.

6.2 Pour the sample into a separatory funnel.

6.3 Add 30 ml of Freon-113 to the sample bottle and rotate the bottle to rinse the sides. Transfer the solvent to the separatory funnel. Extract by shaking vigorously for 2 min. Allow the layers to separate.

6.4 Tare a distilling flask (predried in an oven at 103°C and stored in a desiccator) and filter the solvent layer into the flask through a funnel containing solvent-moistened filter paper.

Note:

An emulsion that fails to dissipate can be broken by pouring about 1 g Na_2SO_4 into the filter paper cone and draining the emulsion through the salt. Additional 1-g portions can be added to the cone as required.

6.5 Repeat steps 6.3 and 6.4 twice with additional 30-ml portions of fresh solvent, combining all solvent in the distilling flask.

6.6 Rinse the top of the separatory funnel, the filter paper, and the funnel with a total of 20 ml of Freon-113 and collect the washings in the flask.

6.7 Evaporate the solvent from the extraction flask in a water bath at 70°C. Dry by placing the flask on a covered 80°C water bath for 15 min. Draw air through the flask using an applied vacuum for 1 min.

6.8 Cool in desiccator for 30 min and weigh.

7. Calculation

$$\text{Oil and grease} = \frac{R - B}{V}, \quad \text{mg/liter},$$

where

R = residue which is the gross weight of extraction flask minus the tare, mg,

B = blank determination, residue from an equivalent volume of extraction solvent, mg,

V = volume of sample, determined by refilling sample bottle to calibration line and correcting for acid addition if necessary, liters.

8. Precision and Accuracy

The oil and grease content of a sewage sample was determined to be 12.6 mg/liter. When 1-liter portions of the sewage were dosed with

14.0 mg of a mixture of No. 2 fuel oil and Wesson Oil, the recovery was 93% with a standard deviation of 0.9 mg.

Working Bibliography for Sect. 4.20

K. A. Blum and M. J. Taras, "Determination of Emulsifying Oil in Industrial Wastewater", JWPCF Research Suppl. 40, R404 (1968).

Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, p. 229 (1976).

Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 515, Method 502A (1975).

4.21 Analytical Procedures for Total Oil and Grease, Infrared Method (performed by Environmental Analysis Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

1.1 This method includes the measurement of Freon-extractable matter from surface and saline waters and from industrial and domestic wastes. It is applicable to the determination of hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and related matter.

1.2 The method is applicable to measurement in water of most light petroleum fuels, although loss of about one-half of any gasoline present during the extraction manipulations can be expected.

1.3 The method detects from 2.0 to 1000 mg/liter of extractable material.

2. Summary of Method

2.1 The sample is acidified to a low pH (<2) and extracted with Freon. The oil and grease is determined by comparison of the infrared absorbance of the sample extract with standards.

2.2 Carbon tetrachloride (CCl_4) or other suitable solvents may be substituted for Freon when very low detection limits are required or the purity of the available Freon is unsatisfactory. Proper safety precautions should be taken when using CCl_4. Using a 1-liter sample, the lowest concentration reported is 2.0 mg/liter.

2.3 The degree of extraction of the grease and oil depends on the procedure used. The source of the oil and/or grease and the presence of extractable nonoily matter will influence the material measured and interpretation of results.

2.4 An "unknown oil" is defined as one for which a representative sample of the oil or grease is not available for preparation of a standard. Examples of unknown oils are the oil and grease in a mixed sewage or an unidentified oil slick on a surface water.

2.5 A "known oil" is defined as a sample of oil and/or grease that represents the only material of that type used or manufactured in the processes represented by a wastewater.

3. Sample Handling and Preservation

3.1 A representative 1-liter sample should be collected in a glass bottle. If analysis is to be delayed for more than a few hours, the sample should be preserved by the addition of 5 ml H_2SO_4 or HCl (see step 5.1) at the time of collection.

3.2 Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. Individual portions collected at prescribed time intervals must be analyzed separately to obtain the average concentration over an extended period.

4. Apparatus

4.1 Separatory funnel, 2000-ml, with Teflon stopcock

4.2 Infrared spectrophotometer, double-beam, recording

4.3 Cells, quartz, 10-mm, 50-mm, and 100-mm path length

4.4 Syringes, 10-, 25-, 50-, and 100-microliter capacity

4.5 Filter paper, Whatman No. 40, 11-cm

5. Reagents

5.1 Sulfuric acid (H_2SO_4), 1:1. Mix equal volumes of concd H_2SO_4 and distilled water. (Concd hydrochloric acid may be substituted directly for concd H_2SO_4 for this reagent.)

5.2 Freon-113, (bp 48°C), 1,1,2-trichloro-1,2,2-trifluoroethane. At this time, reagent-grade Freon is not available commercially. Freon-113 is available from E. I. DuPont de Nemours, Inc., and distributed in 5-gal cans. It is best handled by filtering 1-gal quantities through paper into glass containers. A regular program of solvent blank monitoring should be maintained.

5.3 Carbon tetrachloride (CCl_4), reagent grade

5.4 Sodium sulfate (Na_2SO_4), anhydrous crystal

5.5 Known oil reference standard: Accurately weigh about 0.05 g of known oil directly into a 100-ml volumetric flask. Add 80 ml

Freon to dissolve the oil. If, as in the case of a heavy fuel oil, all the oil does not go into solution, allow to stand overnight. The next day, filter through paper into another 100-ml volumetric flask and dilute to mark. For calculations, assume all oil had gone into solution.

5.6 Unknown oil reference standard (10 microliters = 7.69 mg oil): Pipette 15 ml n-hexadecane, 15 ml isooctane, and 10 ml benzene into a 50-ml glass-stoppered bottle. Assume the specific gravity of this mixture to be 0.769 and maintain the integrity of the mixture by keeping stoppered except when withdrawing aliquots.

6. Procedure

6.1 Mark the sample bottle at the water meniscus for later determination of sample volume. If the sample was not acidified at time of collection, add 5 ml of H_2SO_4 (see step 5.1) to the sample bottle. After mixing the sample, check the pH by touching pH-sensitive paper to the cap to make certain that the pH is 2 or lower. Add more acid if necessary.

6.2 Pour the sample into a separatory funnel.

6.3 Add 30 ml of Freon to the sample bottle (see step 5.2) and rotate the bottle to rinse the sides. Transfer the Freon into the separatory funnel. Extract by shaking vigorously for 2 min. Allow the layers to separate.

6.4 Filter the solvent layer into a 100-ml volumetric flask through a funnel containing solvent-moistened filter paper. An emulsion that fails to dissipate can be broken by pouring about 1 g Na_2SO_4 (step 5.4) into the filter paper cone and draining the emulsion through the salt. Additional 1-g portions can be added to the cone as required.

6.5 Repeat steps 6.3 and 6.4 twice more with 30-ml portions of fresh solvent, combining all solvent in the volumetric flask.

6.6 Rinse the tip of the separatory funnel, filter paper, and the funnel with a total of 10 to 20 ml Freon and collect the rinsings in the flask. Dilute the extract to 100 ml and stopper the flask.

6.7 Select the appropriate calibration standards and cell pathlength according to the following table of approximate working ranges:

Pathlength	Range
1 cm	4 to 40 mg
5 cm	0.5 to 8 mg
10 cm	0.1 to 4 mg

Prepare calibration standards by pipetting appropriate amounts of the known oil reference standard (step 5.5) into 100-ml volumetric flasks and diluting to mark with Freon. Alternately, transfer appropriate amounts of the unknown oil reference standard (step 5.6) using microliter syringes to 100-ml volumetric flasks and dilute to mark with Freon. Ten microliters of the unknown oil is equivalent to 7.69 mg per 100 ml Freon.

6.8 Scan standards and samples from 3200 cm^{-1} to 2700 cm^{-1} with Freon in the reference beam and record the results on absorbance paper. The absorbances of samples and standards are measured by constructing a straight baseline over the range of the scan, measuring the absorbance of the peak maximum at 2930 cm^{-1}, and subtracting the baseline absorbance at that point. If the absorbance exceeds 0.8 for a sample, select a shorter pathlength or dilute as required. Caution must be exercised in the selection of the 2930 cm^{-1} peak because it may not always be the largest peak in the range of the scan. (For an example of a typical oil spectrum and baseline construction see Gruenfeld — Working Bibliography for Sect. 4.20.)

6.9 Use a calibration plot of absorbance versus milligram of oil prepared from the standards to determine the mg of oil in the sample solution.

7. Calculation

Total oil and grease = $\frac{RD}{V}$, mg/liter ,

where

R = oil in solution, determined from calibration plot, mg,

D = extract dilution factor, if needed,

V = volume of sample determined by refilling sample bottle to calibration line and correcting for acid addition if necessary, liters.

8. Precision and Accuracy

This method determined the oil and grease level in a sewage sample to be 17.5 mg/liter. When 1-liter portions of the sewage were dosed with 14.0 mg of a mixture of No. 2 fuel oil and Wesson Oil, the recovery was 99% with a standard deviation of 1.4 mg.

Working Bibliography for Sect. 4.21

American Petroleum Institute, *Manual on Disposal of Refinery Wastes*, Vol. IV, Method 733-58 (1958).

M. Gruenfeld, "Extraction of Dispersed Oils from Water by Quantitative Analysis by Infrared Spectroscopy," *Environmental Science and Technology*, 7, p. 636 (1973).

Manual of Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, p. 232 (1976).

Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 516, Method 502B (1975).

4.22 Determination of Nitrogen (Ammonia), Distillation-Colorimetric Method

(performed by Environmental Analysis Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

1.1 This method covers the determination of ammonia-nitrogen (NH_3-N) exclusive of total Kjeldahl nitrogen in drinking, surface, and saline waters and in domestic and industrial wastes.

1.2 The method as written covers the range from about 0.05 to 2.0 mg/liter NH_3-N. Adjustments in sample size, dilutions, and varying aliquots will allow extension of the range. The lowest concentration of NH_3-N reported is 0.2 mg/liter.

1.3 This method is described for macro-glassware; however, micro-distillation equipment may be used.

2. Summary of Method

2.1 The sample, pretreated to avoid interferences from chlorine or mercury, is buffered at a pH of 9.5 with a borate buffer to decrease hydrolysis of cyanates and organic nitrogen compounds and is distilled into a solution of boric acid. After dilution of the distillate to a known volume, aliquots of a suitable size are withdrawn. Nessler reagent is added, and volume is adjusted to 50 ml in volumetric flasks. The absorbance of the resulting solutions is measured at 425 nm, and the amount of NH_3-N present is determined by comparison with known standards.

2.2 Using a 500-ml sample, the lowest concentration of NH_3-N reported is 0.2 mg/liter.

3. Sample Handling and Preservation

Samples may be preserved with 2 ml of concd H_2SO_4 or 40 mg $HgCl_2$ per liter and storing at 4°C.

4. Interferences

4.1 A number of aromatic and aliphatic amines, as well as other organic and inorganic compounds, will cause turbidity upon the

addition of Nessler reagent. For this reason, direct Nesslerization (i.e., with distillation) has been discarded as an official method.

4.2 Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent even at the 9.5 pH at which the distillation is carried out. Volatile alkaline compounds such as certain ketones, aldehydes, and alcohols may produce an off-color upon Nesslerization in the distillation method. Some of these, such as formaldehyde, may be boiled off at a low pH (about 2 to 3) before distillation and Nesslerization.

4.3 Residual chlorine must also be removed by pretreatment of the sample with sodium thiosulfate before distillation.

4.4 If the sample has been preserved with a mercury salt, the mercury ion must be complexed with sodium thiosulfate (0.2 g) before distillation.

5. Apparatus

5.1 An all-glass distilling apparatus with a 1000-ml flask and a condenser. The condenser should either be mounted in a vertical position or have a bent delivery tip to allow the immersion of the tip in the receiving flask.

5.2 Spectrophotometer or filter photometer for use at 425 nm and providing a light path of 1 cm or more

5.3 Spectrophotometer cells: Matched cells of 1 to 5 cm, as required.

5.4 Erlenmeyer flasks: The distillate is collected in 500-ml glass-stoppered flasks. These flasks should be marked at the 350- and the 500-ml volumes making transfer of the distillate to volumetric flasks unnecessary.

5.5 50-ml volumetric flasks

5.6 Various sizes of pipettes

6. Reagents

6.1 All solutions must be made with ammonia-free distilled water. If necessary, ammonia can be removed by passage through an appropriate ion exchange column.

6.2 Ammonium chloride (NH_4Cl), stock solution: 1 ml = 1 mg NH_3-N. Dissolve 3.819 g of dry NH_4Cl in distilled water and bring to volume in a 1-liter volumetric flask.

6.3 Ammonium chloride (NH_4Cl), standard solution: 1 ml = 0.01 mg. Dilute 10 ml of stock solution (step 6.2) to 1 liter in a volumetric flask.

6.4 Boric acid solution (20 g/liter): Dissolve 20 g H_3BO_3 in ammonia-free distilled water and dilute to 1 liter. A 50-ml portion of this solution is sufficient for up to 1 mg of ammonia in the distillate.

6.5 Nessler's reagent: Dissolve 100 g of mercuric iodide ($HgCl_2$) and 70 g of potassium iodide (KI) in a small amount of water. Add this mixture slowly, while stirring, to a cooled solution of 160 g of sodium hydroxide (NaOH) in 500 ml of water. Dilute the mixture to 1 liter. If this reagent is stored in a Pyrex bottle out of direct sunlight, it will remain stable for a period of up to 1 year.

6.6 Borate buffer, pH 9.5: Add 88 ml of 0.1 N NaOH solution to 500 ml of 0.025 M sodium tetraborate solution (5.0 g anhydrous $Na_2B_4O_7$, or 9.5 g $Na_2B_4O_7 \cdot 10\ H_2O$, per liter) and dilute to 1 liter.

6.7 Sodium hydroxide, 1 N: Dissolve 40 g NaOH in ammonia-free water and dilute to 1 liter.

6.8 Dechlorinating reagents: A number of dechlorinating reagents may be used to remove residual chlorine prior to distillation. One milliliter of each of the following solutions will remove 1 mg/liter of residual chlorine in 500 ml of sample. The thiosulfate solution is unstable and should be prepared fresh for use. The arsenite solution is stable.

a. Sodium thiosulfate (1/70 N): Dissolve 3.5 g $Na_2S_2O_3$ in distilled water and dilute to 1 liter.

b. Sodium arsenite (1/70 N): Dissolve 1.0 g $NaAsO_2$ in distilled water and dilute to 1 liter.

7. Preparation of Standards and Calibration

7.1 Prepare several standards by taking suitable aliquots from the NH_3-N standard solution(s), adding 1 ml of Nessler's reagent, and diluting to 50 ml in volumetric flasks. After 20 min, read the absorbances of these solutions in the spectrophotometer against a blank solution. From the values obtained, plot absorbance versus mg NH_3-N for the standard curve. Values of standards chosen should encompass the range expected for the samples. The selection of cell path-length should be governed by the amount of NH_3-N present.

8. Procedure

8.1 Preparation of equipment: Add 500 ml of distilled water to the distillation flask. The addition of boiling chips that have been previously treated with dilute NaOH will prevent bumping. Steam out the distillation apparatus until the distillate shows no trace of ammonia with Nessler reagent.

Sample preparation: Remove the residual chlorine in the sample by adding dechlorinating agent equivalent to the chlorine residual. To 500 ml of sample add 1 N NaOH (step 6.7) until the pH is 9.5, checking the pH during addition with a pH meter or by use of a short-range pH paper.

8.2 Distillation: Transfer 500 ml or a suitable aliquot of the sample, the pH of which has been adjusted to 9.5, to the distillation flask and add 25 ml of the borate buffer (step 6.6). Distill 300 ml at the rate of 6 to 10 ml/min into 50 ml of 2% H_3BO_3 (step 6.4) contained in a 500-ml Erlenmeyer flask. The condenser tip, or an extension of the condenser tip, must extend below the level of the H_3BO_3 solution. Dilute the distillate to 500 ml with distilled water.

8.3 Spectrophotometer determination: Determine the ammonia in the distillate by adding an aliquot of the distillate and 1.0 ml of Nessler's reagent to the 50-ml volumetric flask. Dilute each

flask to 50 ml with distilled water and mix. After 20 min, read the absorbance at 425 nm against the blank. From the values, obtain the ammonia-nitrogen content from the standard curve.

9. Calculations

$$NH_3\text{-}N = \frac{AB}{CD} \times \frac{1000 \text{ ml}}{\text{liter}}, \quad \text{mg/liter},$$

where

A = NH_3-N reading from calibration curve, mg,

B = total distillate collected, including H_3BO_3 and dilution, ml,

C = distillate taken for Nesslerization, ml,

D = volume of original sample, ml.

10. Precision and Accuracy

Twenty-four analysts in 16 laboratories analyzed natural water samples containing exact increments of an ammonium salt (Table 4.22-1).

Table 4.22-1. Data on the increments of ammonium salts in water samples

Increment	Precision	Accuracy	
Nitrogen, ammonia (mg/liter)	Standard deviation (mg/liter)	Bias (%)	Bias (mg/liter)
0.21	0.122	-5.54	-0.01
0.26	0.070	-18.12	-0.05
1.71	0.244	+0.46	+0.01
1.92	0.279	-2.01	-0.04

Working Bibliography for Sect. 4.22

Manual of Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, p. 159 (1976).

Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 407 (1975).

4.23 Analytical Procedures for Phenols in Water, Distillation/4-AAP Method

(performed by Environmental Analysis Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

1.1 This method is applicable to the analysis of drinking, surface, and saline waters and of domestic and industrial wastes. It is not possible to differentiate among kinds of phenols by this method. The results of the procedure represent the minimum concentration of phenolic compounds present.

1.2 The range of the method is 0.5 to 50 μg of phenols. The lowest concentration of phenols reported when a 500-ml sample is used is 0.001 mg/liter.

2. Summary of Method

2.1 Phenols are separated from nonvolatile impurities by distillation from an acidic solution containing copper sulfate ($CuSO_4$). The distillate is reacted with 4-aminoantipyrine in the presence of potassium ferricyanide [$K_3Fe(CN)_6$] to form a yellow antipyrine dye, which is extracted from the aqueous solution with chloroform. The absorbance of the organic phase is measured and the amount of phenols present is determined from a calibration curve.

3. Sample Handling and Preservation

Add phosphoric acid (H_3PO_4) to pH <4 and add 1 g $CuSO_4$ per liter. Cool and hold at 4°C no longer than 24 h.

4. Interferences

4.1 Oxidizing agents such as chlorine can be removed by the addition of excess ferrous sulfate ($FeSO_4$).

4.2 Interferences from sulfur compounds are eliminated by adding $CuSO_4$ and acidifying the sample to a pH of <4 with H_3PO_4 while stirring.

5. Apparatus

5.1 Spectrophotometer suitable for measurements at 460 nm, equipped with 1- and 5-cm cells

5.2 Distillation apparatus, all glass with 1-liter distilling flasks, condensers, and electric heaters

5.3 Separatory funnels, 1-liter capacity

5.4 Graduated 800-ml beakers

5.5 pH meter with associated glass and reference electrodes

6. Reagents

6.1 Copper sulfate solution: Dissolve 100 g of reagent-grade copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) in distilled water and dilute to 1 liter.

6.2 Phosphoric acid solution: Dilute 10 ml of concd H_3PO_4 to 100 ml with distilled water.

6.3 Ammonium chloride solution: Dissolve 50 g of reagent-grade ammonium chloride (NH_4Cl) in distilled water and dilute to 1 liter.

6.4 Aminoantipyrine solution: Dissolve 2 g of 4-aminoantipyrine in distilled water and dilute to 100 ml. Prepare fresh daily.

6.5 Potassium ferricyanide solution: Dissolve 8 g of reagent-grade potassium ferricyanide [$K_3Fe(CN)_6$] in distilled water and dilute to 100 ml; filter if necessary. Prepare fresh daily.

6.6 Chloroform ($CHCl_3$), reagent-grade

6.7 Sodium sulfate (Na_2SO_4), anhydrous, reagent-grade

6.8 Stock phenol solution: Dissolve 1 g of reagent-grade phenol (C_6H_5OH) in freshly boiled and cooled distilled water and dilute to 1 liter; 1 ml = 1 mg phenol.

6.9 Intermediate phenol solution: Dilute 10 ml of stock solution (step 6.8) to 1 liter with freshly boiled and cooled distilled water; 1 ml = 10 µg phenol. Prepare a fresh solution on each day of use.

6.10 Standard phenol solution: Dilute 50 ml of the intermediate solution (step 6.9) to 500 ml with freshly boiled and cooled distilled water; 1 ml = 1 µg phenol. Prepare this solution within 2 h of use.

7. Procedure

7.1 Distill the sample as follows:

7.1.1 Transfer 500 ml of sample to an 800 ml beaker and adjust to approximately pH 4 with H_3PO_4 solution (step 6.2).

7.1.2 Add 5 ml of $CuSO_4$ solution (step 6.1) and mix. If at this point there is not sufficient time to complete the analysis, store the sample at 5 to 10°C and complete the analysis within 24 h after collection.

7.1.3 Transfer the sample to the distillation flask; use an 800-ml graduated beaker as the distillate receiver.

7.1.4 Distill 450 ml of the sample; stop the distillation and, when boiling ceases, add 50 ml of phenol-free distilled water to the distillation flask.

7.1.5 Continue the distillation until a total of 500 ml has been collected.

7.2 Extract and determine the amount of phenol present in the distillate as follows:

7.2.1 Prepare a blank by processing 500 ml of distilled water through steps 7.1.1 through 7.1.5 of the procedure. Prepare one of two series of 500 ml phenol standards. If the amount of phenol present is estimated to be low, prepare a series containing 1 µg of phenol and use 5 cm cells to finally determine the phenol present. If the amount of phenol present is estimated to be >10 µg, prepare a standard series containing 10 µg through 50 µg of phenol and use 1 cm cells. Treat samples, blank, and standards alike.

7.2.2 Add 10 ml of NH_4Cl solution to the sample and adjust to pH 10.0 ± 0.2 with concd NH_4OH.

7.2.3 Transfer the solution to a 1-liter separatory funnel; add 3 ml of aminoantipyrine solution and mix well.

7.2.4 Add 3 ml of $K_3Fe(CN)_6$ solution (step 6.5), mix well, and allow the color to develop for 3 min. The solution should be clear and light yellow.

7.2.5 Immediately add 25 ml of chloroform and shake the funnel vigorously 15 times; allow the chloroform to settle and shake again 10 times; allow the chloroform to settle.

7.2.6 Filter the chloroform through dry filter paper containing a 5-g layer of anhydrous Na_2SO_4.

7.2.7 Transfer the chloroform to dry 1- or 5-cm cells (if the sample is estimated to contain less than 10 µg of phenol, use 5-cm cells) and read the absorbance at 460 nm on all samples and standards using the reagent blank as the reference.

7.2.8 Determine the amount of phenol present from a calibration curve.

8. Calculation

$$\text{Phenol} = \frac{\mu\text{g phenol from curve}}{\text{ml sample}} \text{ , mg/liter ,}$$

9. Precision and Accuracy

The precision (95% control limit) in the 5- to 50-µg range is ± 10% of the value, based on the use of C_6H_5OH as the standard. It is impossible to express the accuracy of the method because the phenolic value varies with the types of phenols within a sample.

Working Bibliography for Sect. 4.23

Standard Methods for the Examination of Water and Wastewater, 14th ed., pp. 574-580 (1975).

4.24 Determination of Biochemical Oxygen Demand

(performed by Environmental Analysis Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

1.1 The biochemical oxygen demand (BOD) is a measure of the oxygen required to stabilize the organic matter in a wastewater sample in a given time and at a given temperature. It is probably the best single test for determining the amount of organic matter in wastewater that is subject to biological degradation.

1.2 The biochemical oxygen demand (BOD) determination described herein is an empirical test in which stabilized laboratory procedures are used to determine the relative oxygen requirements of wastewaters, effluents, and polluted waters. The test has its widest application in measuring waste loadings to treatment plants and in evaluating the efficiency (BOD removal) of such treatment systems. BOD values cannot be compared unless the results have been obtained under identical test conditions. The test is of limited value in measuring the actual oxygen demand of surface waters. The extrapolation of test results to actual stream oxygen demands is highly questionable because the laboratory environment does not reproduce stream conditions such as temperature, sunlight, biological population, water movement, and oxygen concentration.

2. Summary of Method

2.1 The dissolved oxygen (DO) content of the sample (or portion thereof) is determined on the day received. The sample (or portion thereof) is then incubated in an airtight container at 20°C for 5 days. The dissolved oxygen content is again determined. The difference in dissolved oxygen content is the BOD for 5 days at 20°C, commonly expressed as BOD_5.

2.2. The oxidative reactions involved in the BOD test are a result of biological activity, and the rate at which the reactions proceed is governed to a large extent by biological population

density and temperature. Temperature effects are held constant by performing the test at 20°C. Experience has shown that a reasonably large percentage of the total BOD is exerted in 5 days.

2.3 The dissolved oxygen (DO) content of the sample, both before and after incubation, can be measured by either of two techniques:

2.3.1 Azide Modified Indometric Method (from *Standard Methods for the Analysis of Water and Wastewater*), or

2.3.2 Membrane Probe Method (from *Environmental Effluent Analysis Manual*).

2.4 The lowest concentration detected and recorded by these methods is 5 mg/liter.

3. Sampling Handling and Preservation

3.1 Samples for BOD analysis may undergo significant degradation during handling and storage. Some of the demand may be satisfied if the sample is held for several days before the test is initiated, resulting in a low estimation of the BOD. The extent of change appears to be a function of the amount of organic matter (food supply) and the number and types of organisms (biological population). To reduce the change in oxygen demand that occurs between sampling and testing, keep all samples at or below 4°C and begin incubation not more than 24 h after the sample is collected.

3.2 The amount of oxygen demand in the sample will govern the need for and the degree of dilution.

3.3 Aerate samples with low DO values to increase the initial DO content above that required by the BOD. Let air bubble through a diffusion tube into the sample for 5 min or until the DO is at least 7 mg/liter. Determine DO on one portion of the aerated sample; seed another portion, if necessary, and incubate for the BOD determination.

4. Apparatus

4.1 Incubation bottles, 300-ml capacity, with ground-glass stopper. Clean bottles with a good detergent, rinse thoroughly, and drain before use. Use a water seal as a precaution against drawing air into the dilution bottle during incubation. Satisfactory water seals are obtained by inverting the bottles in a water bath or adding water to the flared mouth of special BOD bottles.

4.2 Air incubator or water bath, thermostatically controlled (20°C ±1°C): Exclude all light to prevent formation of DO by algae in the sample.

4.3 Graduated cylinders

4.4 Agitating plunger

4.5 Volumetric pipettes

4.6 Mohr pipettes

4.7 Burette

4.8 Reagent bottles

4.9 5-gal carboy bottles

4.10 Glass and plastic tubing

4.11 Membrane probe DO meter (optional)

4.12 Analytical balance

4.13 pH meter

4.14 Refrigerator

5. Reagents

5.1 Distilled water: Use only high-quality water distilled from a block tin or all-glass still. Alternatively, use deionized water. The water must contain less than 0.01 mg/liter copper and be free of chlorine, chloramines, caustic alkalinity, organic material, and acids.

5.2 Phosphate buffer solution: Dissolve 8.5 g potassium dihydrogen phosphate (KH_2PO_4), 21.75 g dipotassium hydrogen phosphate (K_2HPO_4), 33.4 g disodium hydrogen phosphate heptahydrate ($Na_2HPO_4 \cdot 7H_2O$), and 1.7 g ammonium chloride (NH_4Cl) in about

500 ml distilled water and dilute to 1 liter. The pH of this buffer should be 7.2 without further adjustment. Discard the reagent (or any of the following reagents) if there is any sign of biological growth in the stock bottle.

5.3 Magnesium sulfate solution: Dissolve 22.5 g $MgSO_4 \cdot 7H_2O$ in distilled water and dilute to 1 liter.

5.4 Calcium chloride solution: Dissolve 27.5 g anhydrous $CaCl_2$ in distilled water and dilute to 1 liter.

5.5 Ferric chloride solution: Dissolve 0.25 g $FeCl_3 \cdot 6H_2O$ in distilled water and dilute to 1 liter.

5.6 Acid and alkali solutions, 1 N: For neutralization of caustic or acidic waste samples.

5.7 Sodium sulfite solution, 0.025 N: Dissolve 1.575 g anhydrous Na_2SO_3 in 1000 ml of distilled water. This solution is not stable; prepare daily.

5.8 Seeding: Seeding is done to introduce into the sample a biological population capable of oxidizing the organic matter in the wastewater. Where such microorganisms are already present, as in domestic wastewater or unchlorinated effluents and surface waters, seeding is unnecessary and should not be used.

When the sample contains very few microorganisms — as a result, for example, of chlorination, high temperature, or extreme pH — seed the dilution water. The standard seed material is settled domestic wastewater that has been stored at 20°C for 24 to 36 h. Use sufficient seed to produce a seed correction of at least 0.6 mg/liter.

6. Procedure

6.1 Preparation of dilution water.

6.1.1 Before use, store the distilled water in cotton-plugged bottles long enough for it to become saturated with DO. If such storage is not practical, saturate the water either by shaking the partially filled bottle or by aeration with a supply of clean compressed air. Use distilled water at 20°C ± 1°C.

6.1.2 Place the desired volume of distilled water in a suitable bottle and add 1 ml each of phosphate buffer, $MgSO_4$, $CaCl_2$, and $FeCl_3$ solutions for each liter of water. If dilution water is to be stored in the incubator, add the phosphate buffer just before using the dilution water.

6.2 Seeding. See step 5.8 preceding. If the dilution water is seeded, use it the day it is prepared.

6.3 Pretreatment.

6.3.1 Samples containing caustic alkalinity or acidity. Neutralize to about pH 7.0 with 1N H_2SO_4 or NaOH, using a pH meter or bromthymol blue as an outside indicator. The pH of the seeded dilution water will not be changed by the preparation of the lowest dilution of sample.

6.3.2 Samples containing residual chlorine compounds. If the samples stand for 1 to 2 h, the residual chlorine often will be dissipated. Prepare BOD dilutions with properly seeded standard dilution water. Destroy higher chlorine residuals in neutralized samples by adding Na_2SO_3. Determine the appropriate quantity of sodium sulfite solution on a 100- to 1000-ml portion of the sample by adding 10 ml of 1 + 1 acetic acid or 1 + 50 H_2SO_4, followed by 10 ml of KI solution (100 ml = 10 g) and titrating with 0.025N Na_2SO_3 solution to the starch-iodide end point. Add to a volume of sample the quantity of Na_2SO_3 solution determined by the above test, mix, and after 10 to 20 min, test a sample for residual chlorine to check the treatment. Prepare BOD dilutions with seeded standard dilution water.

6.3.3 Samples containing other toxic substances, such as toxic metals from industrial plating wastes, frequently require special treatment.

6.3.4 Samples supersaturated with DO. Samples containing more than 9 mg/liter DO at 20°C may be encountered during

winter months or in localities where algae are growing actively. To prevent loss of oxygen during incubation of these samples, reduce the DO to saturation by bringing the sample to about 20°C in a partly filled bottle and agitating it by vigorous shaking or by aerating with compressed air.

6.4 Dilution technique.

6.4.1 Make several dilutions of the prepared sample to obtain the suggested diltions: 0.1 to 1.0% for strong trade wastes, 1 to 5% for raw and settled sewage, 5 to 25% for oxidized effluents, and 25 to 100% for polluted river waters.

6.4.2 Siphon carefully (to avoid entrainment of air) standard dilution water, seeded if necessary, into a graduated cylinder of 1000- to 2000-ml capacity, filling the cylinder half full. Add the carefully mixed sample to make the desired dilution and dilute to the appropriate level with dilution water. Mix well with a plunger-type mixing rod, avoiding entrainment of air. Siphon the mixed dilution into two BOD bottles, one for incubation and the other for determination of the initial DO in the mixture. Prepare succeeding dilutions in the same manner or by adding dilution water to the unused portion of the preceding dilution.

6.4.3 The dilution technique can be simplified by pipetting a suitable amount of the sample directly into BOD bottles of known capacity. The bottles are filled with sufficient dilution water to allow insertion of the stopper without leaving air bubbles. If dilutions greater than 1:100 are needed, make a preliminary dilution in a volumetric flask and then make the necessary final dilution into the BOD bottle.

6.4.4 If the membrane-probe DO meter is used, the initial DO and the incubated DO can be determined on the same sample, thus eliminating the need for duplicate dilutions. The

probe will displace only a small amount of the sample from the bottle. After the probe is removed from the bottle, a glass marble is placed in the bottle, restoring the sample to its original level. The bottle is then stoppered and sealed for incubation. Plastic caps are available that fit snugly over the neck of the BOD bottle to provide an airtight seal and allow the bottle to be stored upright in the incubator.

6.5 Determination of DO: If the sample represents 1% or more of the lowest BOD dilution, determine DO on the undiluted sample. This determination is usually omitted on sewage and settled effluents known to have a DO content of practically zero. With samples having an immediate oxygen demand, use a calculated initial DO because such a demand represents a load on the receiving water.

6.6 Incubation: Incubate the blank dilution water and the diluted samples for 5 days in the dark at 20°C. Then determine the DO in the incubated samples and the blank using the azide modification of the iodometric method or a membrane electrode. Unless the membrane electrode is used, use the alum-flocculation method for incubated samples of muds and the copper sulfate-sulfamic acid method for activated sludges. In special cases, other modifications may be necessary. Those dilutions showing a residual DO of at least 1 mg/liter and a depletion of at least 2 mg/liter are most reliable.

6.7 Seed correction: If the dilution water is seeded, determine the oxygen depletion of the seed by setting up a separate series of seed dilutions and selecting those resulting in 40 to 70% oxygen depletions in 5 days. Use one of these depletions to calculate the correction resulting from the amount of seed in the dilution water. Do not use the seeded blank for seed correction because the 5-day seeded dilution water blank is subject to erratic oxidation because of the very high dilution of seed. This problem is not encountered, however, in the seeded sample.

6.8 Dilution water control: Fill two BOD bottles with unseeded dilution water. Stopper and water-seal one of these for incubation. Determine the DO before incubation in the other bottle. Use the DO results on these two bottles as a rough check on the quality of the unseeded dilution water. Do not use the depletion obtained as a blank correction; it should not be more than 0.2 mg/liter and preferably not more than 0.1 mg/liter.

6.9 Glucose-glutamic acid check.

6.9.1 The quality of the dilution water, the effectiveness of the seed, and the technique of the analyst should be checked periodically by using pure organic compounds having known or determinable BOD. If a particular organic compound is known to be present in a given waste, it may well serve as a control on the seed used. For general BOD work, a mixture of glucose and glutamic acid (150 mg/liter of each) has certain advantages. Glucose has an exceptionally high and variable oxidation rate with relatively simple seeds. When it is used with glutamic acid, the oxidation rate is stabilized and is similar to that obtained with many municipal wastes (0.16 to 0.19 exponential rate). In exceptional cases a given component of a particular waste may be the best choice to test the efficacy of a particular seed.

6.9.2 To check the dilution water, the seed material, and the technique of the analyst, prepare a standard solution containing 150 mg/liter each of reagent-grade glucose and glutamic acid that have been dried at 103°C for 1 h. Pipette 5 ml of this solution into calibrated incubation bottles, fill with seeded dilution water, and incubate with seed control at 20°C for 5 days. On the basis of a mixed primary standard containing 150 mg/liter each of glucose and glutamic acid, the 5-day BOD varies in magnitude according to the type seed and precision varies with the quality of seed.

7. Calculation

7.1 Definitions

7.1.1 DO = Dissolved oxygen

7.1.2 D_0 = DO of original dilution water

7.1.3 D_1 = DO of diluted sample 15 min after preparation

7.1.4 D_2 = DO of diluted sample after incubation

7.1.5 S = DO of original undiluted sample

7.1.6 D_c = DO available in diluted sample at zero time = $D_0p + SP$

7.1.7 p = decimal fraction of dilution water in diluted sample

7.1.8 P = decimal fraction of original sample in diluted sample

7.1.9 B_1 = DO of dilution of seed control before incubation

7.1.10 B_2 = DO of dilution of seed control after incubation

7.1.11 f = ratio of seed in sample to seed in control

$$= \frac{\% \text{ seed in } D_1}{\% \text{ seed in } B_1}$$

7.1.12 Seed correction = $(B_1 - B_2)f$

7.2 Biochemical oxygen demand (BOD)

7.2.1 When seeding is not required,

$$\text{BOD} = \frac{D_1 - D_2}{P}, \quad \text{mg/liter}.$$

7.2.2 When using seeded dilution water,

$$\text{BOD} = \frac{(D_1 - D_2)\ (B_1 - B_2)f}{P}, \quad \text{mg/liter}.$$

7.2.3 Including immediate dissolved oxygen demand (IDOD) if small or not determined,

$$\text{BOD, mg/liter} = \frac{D_c - D_2}{P}.$$

7.3 Immediate dissolved oxygen demand (IDOD):

$$\text{IDOD} = \frac{D_c - D_1}{P}, \quad \text{mg/liter}.$$

7.4 The DO determined on the unseeded dilution water after incubation is not used in the BOD calculations because this practice would overcorrect for the dilution water. In all the above calculations, corrections are not made for small losses of DO in the dilution water during incubation because proper corrections are difficult and the results are questionable.

8. Precision and Accuracy

8.1 Currently, no standard exists against which the accuracy of the BOD test can be measured. To obtain interlaboratory precision data, a glucose-glutamic acid mixture with a theoretical oxygen demand value of 194 mg/liter was analyzed by 73 participants. Each laboratory used its own seed material. The arithmetic mean of all results was 175 mg/liter, and the standard deviation of that mean was ± 26 mg/liter (15%).

Working Bibliography for Sect. 4.24

Manual of Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, p. 11 (1976).

Standard Methods for the Analysis of Water and Wastewater, 14th ed., p. 543, Method 507 (1975).

4.25 Determination of Chemical Oxygen Demand (Low Level), Titration Method

(performed by Environmental Analysis Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

   1.1 The Chemical Oxygen Demand (COD) method determines the quantity of oxygen required to oxidize the organic matter in a waste sample under specific conditions of oxidizing agent, temperature, and time.

   1.2 This method (low level) is applicable for samples having a COD in the range of 5 to 50 mg/liter.

2. Summary of Method

   2.1 Organic and oxidizable inorganic substances in an aqueous sample are oxidized by potassium dichromate ($K_2Cr_2O_7$) solution in 50% (by volume) sulfuric acid (H_2SO_4) solution. The excess dichromate is titrated with standard ferrous ammonium sulfate [$Fe(NH_4)_2(SO_4)_2$] using orthophenanthroline ferrous complex (ferroin) as an indicator.

   2.2 Using a 50-ml sample, the lowest concentration reported for this method is 5 mg/liter.

3. Sample Handling and Preservation

   3.1 Collect the samples in glass bottles, if possible. Use of plastic containers is permissible if it is known that no organic contaminants are present in the containers.

   3.2 Biologically active samples should be tested as soon after collection as possible. Samples containing settleable material should be well mixed (preferably homogenized) to permit removal of representative aliquots.

   3.3 Samples may be preserved by adding 2 ml of concd H_2SO_4 for each liter of sample.

4. Interferences

4.1 Traces of organic material from the glassware or atmosphere may cause gross, positive errors.

4.1.1 Extreme care should be exercised to avoid contamination from organic materials in the distilled water used for reagent preparation or sample dilution.

4.1.2 Glassware should be conditioned by repeated execution of the procedure using blank solutions to eliminate traces of organic material.

4.2 Volatile materials may be lost when the sample temperature rises during the sulfuric acid addition step.

4.3 Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion flask to complex the chlorides, thereby effectively eliminating the interference on all but brine and estuarine samples.

4.4 Nitrite interferences are eliminated by an addition of sulfamic acid.

5. Apparatus and Reagents

5.1 Reflux apparatus: Glassware should consist of a 500-ml Erlenmeyer flask or a 300-ml round-bottom flask made of heat-resistant glass connected to a 12-inch Allihn condenser by means of a ground-glass joint. Any equivalent reflux apparatus may be substituted provided that a ground-glass connection is used between the flask and the condenser.

5.2 Distilled water: Special precautions should be taken to ensure that distilled water used in this test is low in organic matter.

5.3 Standard potassium dichromate solution (0.025 N): Dissolve 12.259 g $K_2CR_2O_7$, primary standard grade, that has previously been dried at 103°C for 2 h in distilled water and dilute to 1000 ml. Mix this solution thoroughly. Add 0.12 g of sulfamic acid to a 100-ml aliquot of the solution and dilute to 1000 ml with distilled water.

5.4 Sulfuric acid reagent: Concd H_2SO_4 containing 23.5 g silver sulfate (Ag_2SO_4) per 9 lb bottle. (One to two days are required for dissolution.)

5.5 Standard ferrous ammonium sulfate (0.025 N): Dissolve 98 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in distilled water. Add 20 ml of concd H_2SO_4, cool, and dilute to 1 liter. Dilute 100 ml of this solution to 1 liter with distilled water. This solution must be standardized daily against $K_2Cr_2O_7$ solution as follows.

5.5.1 Standardization: To 15 ml of distilled water, add 10.0 ml of 0.025 N $K_2Cr_2O_7$ solution. Add 20 ml of concd H_2SO_4 and cool. Titrate with 0.025 N $Fe(NH_4)_2(SO_4)_2$ using 1 drop of ferroin indicator. The color change is sharp, going from blue-green to reddish-brown.

$$\text{Normality} = \frac{(\text{ml } K_2Cr_2O_7)(0.025)}{\text{ml } Fe(NH_4)_2(SO_4)_2}$$

5.6 Mercuric sulfate ($HgSO_4$), powdered

5.7 Phenanthroline ferrous sulfate (ferroin) indicator solution: Dissolve 1.48 g of 1 to 10 (ortho) phenanthroline monohydrate, together with 0.70 g of $FeSO_4 \cdot 7H_2O$ in 100 ml of water. This indicator may be purchased already prepared.

5.8 Silver sulfate (Ag_2SO_4), powdered

5.9 Sulfuric acid (H_2SO_4) (sp.gr. 1.84), concentrated

5.10 Sulfamic acid (H_2NSO_3H)

6. Procedure

6.1 Place several boiling chips in the reflux flask, followed by 1 g of $HgSO_4$. Add 5.0 ml concd H_2SO_4; swirl until $HgSO_4$ has dissolved. Place reflux flask in an ice bath and slowly add, with swirling, 25.0 ml of 0.025 N $K_2Cr_2O_7$. Slowly add 70 ml of sulfuric acid-silver sulfate solution (see step 5.4) to the cooled reflux flask and swirl.

6.2 With the reflux flask in the ice bath, place 50.0 ml of the sample, or an aliquot diluted to 50.0 ml, into the reflux flask.

Caution:

Care must be taken to assure that the content of the flask is well mixed. If not, superheating may result and the mixture may be blown out of the open end of the condenser. Attach the flask to the condenser and start the cooling water.

6.3 Apply heat to the flask and reflux for 2 h. For some waste waters, the 2-h reflux period is not necessary. The time required for maximum oxidation of a wastewater of constant or known composition may be determined and a shorter period of refluxing may be permissible.

6.4 Allow the flask to cool and wash the condenser with about 25 ml of distilled water. If a round-bottom flask has been used, transfer the mixture to a 500-ml Erlenmeyer flask, washing the reflux flask three or four times with distilled water. Dilute the acid solution to about 300 ml with distilled water and allow the solution to cool to room temperature. Add eight to ten drops of ferroin indicator to the solution and titrate the excess dichromate with 0.025 N $Fe(NH_4)_2(SO_4)_2$ solution to the end point. The color change will be sharp, changing from a blue-green to a reddish hue.

6.5 Blank: Simultaneously run a blank determination following the details given in steps 6.1 and 6.2, but using low COD water in place of the sample.

7. Calculation

Calculate the COD of the sample as follows:

$$COD = \frac{(B - A)N \times 8000}{S}, \quad \text{mg/liter},$$

where

A = volume of $Fe(NH_4)_2(SO_4)_2$ solution required for titration of the sample, ml,

B = volume of $Fe(NH_4)_2(SO_4)_2$ solution required for titration of the blank, ml,

N = normality of the $Fe(NH_4)_2(SO_4)_2$ solution,

S = volume of sample used for the test, ml.

8. Precision and Accuracy

Eighty-six analysts in 58 laboratories analyzed a distilled water solution containing oxidizable organic material equivalent to 12.3 mg/liter COD. The standard deviation was ±4.15 mg/liter COD with an accuracy, as percent relative error (bias), of 0.3%.

Working Bibliography for Sect. 4.25

Manual of Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protective Agency, pp. 21-24 (1976).

Standard Methods for the Examination of Water and Wastewater, 14th ed., pp. 550-554, Method No. 508 (1975).

4.26 Determination of pH, Electrometric Laboratory Method (performed by Environmental Analysis Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

1.1 This method is applicable to drinking, surface, and saline waters and to domestic and industrial wastes.

2. Summary of Method

2.1 The pH of a sample is an electrometric measurement using either a glass electrode in combination with a reference potential (saturated calomel electrode) or a combination electrode (glass and reference). The range of pH values is usually 4 to 10. Values are reported to 0.1 pH unit.

3. Sample Handling and Preservation

The sample must be analyzed as soon as practical, preferably within a few hours. Do not open sample bottle before analysis. Measurements of pH should always be made onsite if possible.

4. Interferences

Oil and grease may interfere by coating the pH electrode and causing sluggish response.

5. Apparatus

pH meter — a pH meter having associated glass and reference electrodes

6. Reagents

Buffer solutions. Preparation of standard buffer solutions are described in the Working Bibliography. In practice, commercial buffer preparations of pH 4, 7, and 10 are used.

7. Procedure

7.1 Set up and standardize the pH meter according to the manufacturer's instructions.

7.2 At least three buffer solutions must be used initially to standardize the instrument. They should cover the pH range of the samples to be measured.

7.3 Rinse the electrodes thoroughly with distilled water and measure the pH of two successive portions of the sample. The results should differ by no more than 0.1 unit. Record these values.

7.4 Rinse the electrodes and store them in a beaker of distilled water.

8. Calculations

8.1 Because the meter is calibrated in pH units, the pH of the sample is obtained directly from the instrument reading. Average the two results and report the pH value to the nearest 0.1 unit.

9. Precision and Accuracy

9.1 Forty-four analysts in 20 laboratories analyzed six synthetic water samples containing exact increments of hydrogen-hydroxyl ions (Table 4.26-1).

Table 4.26-1. Data on the increments of hydrogen-hydroxyl ions in water samples

Increment (pH units)	Precision	Accuracy	
	Standard deviation (pH units)	Bias (%)	Bias (pH units)
3.5	0.10	-0.29	-0.01
3.5	0.11	-0.00	
7.1	0.20	+1.01	+0.07
7.2	0.18	-0.03	-0.002
8.0	0.13	-0.13	-0.01
8.0	0.12	+0.16	+0.01

9.2 In a single laboratory, using surface water samples at an average pH of 7.2, the standard deviation was ±0.1 pH units.

Working Bibliography for Sect. 4.26

ASTM Standards, Part 31, Water, p. 178, Method D1293-65 (1976).

Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, p. 239 (1976).

Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 460, Method 424 (1975).

4.27 Chromium (VI), Spectrophotometric Method
(performed by Environmental Analysis Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

   1.1 The spectrophotometric method is applicable to the analysis of drinking waters, surface waters, and domestic and industrial wastes.

   1.2 This method is applicable to samples containing 0.01 to 1.0 mg/liter chromium. Upward extension of this range is possible by taking appropriate aliquots of the sample waters and diluting to give concentration in the desired range or by using a cell with a shorter path.

2. Summary of Method

   2.1 Chromium (VI) reacts with diphenylcarbazide in acidic medium to produce a red-violet coloration of unknown composition suitable for colorimetric determination of low concentrations of chromium.

   2.2 Using a 50-ml sample, the lowest concentration reported is 0.01 mg/liter.

3. Sampling and Preservation

   3.1 Special care is needed to minimize absorption of chromium on the walls of the sampling container. New, clean, glass bottles rather than old, etched containers should be used for sample collection.

   3.2 Samples should be preserved by filtering through a sintered glass or membrane filter and acidifying with HNO_3 to pH less than 2. The sample should be analyzed the same day as collected. If this is not possible, it should be stored at 4°C.

4. Interferences

   4.1 The reaction with diphenylcarbazide is nearly specific for chromium. Hexavalent molybdenum and mercury salts will react to form color with diphenylcarbazide, but the intensities are much

lower than that for chromium at the specified pH. Concentrations of molybdenum and mercury up to 200 mg/liter can be tolerated.

4.2 Vanadium interferes to a great extent but can be present in a concentration up to ten times that of chromium without causing a problem. The color produced with vanadium fades fairly rapidly and is negligible 10 min after the addition of diphenylcarbazide.

4.3 Ferric iron in concentrations greater than 1 mg/liter can interfere by producing a yellow color with the reagent; however, in the absence of chloride and with sulfuric and phosphoric acid present, the color produced is not strong and poses no problem if measured spectrophotometrically at the appropriate wavelength.

4.4 Turbidity and coloration present in the sample could interfere but are corrected by measuring the absorbance of the sample before and after addition of the chromium color-developing reagent.

4.5 Additional information concerning potential interferences may be found in the references cited in the Working Bibliography for this section.

5. Apparatus

5.1 Spectrophotometer, for use at 540 nm, providing a light path of 2 cm or longer

5.2 Filter, sintered-glass or membrane

6. Reagents

6.1 Stock chromium solution: Dissolve 141.4 mg potassium dichromate ($K_2Cr_2O_7$) in distilled water and dilute to 1 liter; 1.00 ml = 0.050 mg Cr.

6.2 Standard chromium solution: Dilute 10.00 ml stock chromium solution to 100 ml; 1.00 ml = 0.005 mg Cr.

6.3 Double distilled water: Distilled water redistilled in an all-glass apparatus.

6.4 Ammonium hydroxide (NH_4OH), concentrated

6.5 Sulfuric acid (H_2SO_4), 1 + 1: Combine equal volumes of concd H_2SO_4 and distilled water as needed.

6.6 Phosphoric acid (H_3PO_4), 85%, reagent-grade

6.7 Diphenylcarbazide solution: Dissolve 0.25 g 1,5-diphenylcarbazide in 50 ml of acetone. Store in brown bottle. Discard when the solution becomes discolored.

7. Calibration

7.1 Pipette measured volumes of the standard chromium solution (1 ml = 5 µg) ranging from 1.0 to 20.0 ml into 100-ml volumetric flasks.

7.2 Add 2.0 ml of 1 + 1 H_2SO_4 and 0.3 ml (6 drops) 85% H_3PO_4; dilute to near volume with distilled water and mix.

7.3 Add 2.0 ml diphenylcarbazide solution; dilute to volume with distilled water, mix, and allow to stand 5 to 10 min for full color development.

7.4 Measure the absorbance at 540 nm. Use distilled water as a reference. Correct the absorbance readings on the standards by subtracting the absorbance of a reagent blank carried through the procedure. Construct a calibration curve by plotting corrected absorbance versus micrograms of chromium.

8. Procedure

8.1 If sample contains suspended solids, filter a portion of the solution through a sintered-glass or membrane filter.

8.2 Adjust the sample until it is just acidic to litmus paper by adding concd NH_4OH and/or 1 + 1 H_2SO_4 by drops.

8.3 Pipette suitable duplicate aliquots into 100-ml volumetric flasks. Dilute to near volume with distilled water, add 2 ml 1 + 1 H_2SO_4 and 0.3 ml 85% H_3PO_4, and mix.

8.4 To one of the aliquots add 2 ml diphenylcarbazide solution, dilute to volume with distilled water, and mix. Allow to stand 5 to 10 min for color development. Dilute the other aliquot to volume with distilled water and mix.

8.5 Measure the absorbance of the solutions at 540 nm using distilled water as the reference. Correct for absorbance resulting from turbidity and background color by subtracting the absorbance of the aliquot without the diphenylcarbazide from the absorbance of the color-developed aliquot. If deemed necessary, correct for reagent absorbance by carrying known amounts of distilled water and reagents through the color development procedure and measuring against distilled water.

8.6 From the corrected absorbance, determine the amount of chromium present in the sample by reference to the standard calibration curve.

9. Calculation

$$\text{Chromium (VI)} = \frac{R}{V}, \quad \text{mg/liter},$$

where

R = chromium reading from standard curve, µg,
V = volume of sample, ml.

10. Precision and Accuracy

At the Paducah Gaseous Diffusion Plant, for a 20 mg/liter chromium standard, a standard deviation of ± 0.26 mg/liter was obtained for 275 measurements.

Working Bibliography for Sect. 4.27

Foster Dee Snell and Cornelia L. Snell, *Colorimetric Methods of Analysis*, 3rd ed., Vol. II, p. 274 (1949).

Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 192 (1975).

4.28 Determination of Conductance (Specific), Conductivity Meter Laboratory Method

(performed by Environmental Analysis Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

This method is applicable to drinking, surface, and saline waters and to domestic and industrial wastes.

2. Summary of Method

2.1 The specific conductance of a sample is measured by use of a self-contained conductivity meter, Wheatstone bridge-type, or equivalent.

2.2 Samples are preferably analyzed at 25°C. If not, temperature corrections are made and results reported for 25°C.

2.3 The lowest reported value is 0.5 µS (0.5 µmho) for distilled water.

2.4 The instrument is standardized with potassium chloride (KCl) solution daily before use.

3. Interferences

3.1 Conductivity cell must be kept clean.

3.2 Field measurements with comparable instruments are reliable checks.

4. Apparatus and Reagents

4.1 Conductivity meter and associated conductivity cell

4.2 Thermometer, precision, ASTM, range of -2° to 32°C.

4.3 Standard conductivity solutions: Preparation of potassium chloride (KCl) standards is as follows:

4.3.1 Dissolve 745.6 mg of anhydrous KCl in water that has been passed through a mixed-bed deionizer and dilute to 1000 ml at 25°C, (1 ml = 0.7456 mg) to obtain a 0.0100 M solution. This standard has a specific conductance of 1.413 S/cm and is satisfactory for most waters when the cell constant is between 1 and 2.

4.3.2 For other cell constants, stronger or weaker KCl solutions should be used. These are listed in Table 4.28-1.

Table 4.28-1. Conductance of KCl solutions at 25°C

Concentration (moles/liter)	Specific conductance (S/cm)
0.0001	14.94
0.0005	73.90
0.001	147.0
0.005	717.8
0.01	1,413
0.02	2,707
0.05	6,668
0.10	12,900
0.20	24,820
0.50	58,640
1.0	111,900

5. Procedure

5.1 Set up and standardize the conductivity meter according to the manufacturer's instructions.

5.2 Adjust the sample temperature to 25°C ± 0.1°C.

5.3 Rinse the cell with distilled water and several times with the sample to be measured. Measure the conductivity of two successive portions of the sample. The results should agree within 10%. Record these values.

6. Calculations

6.1 Average the sample results. For instruments that measure directly in µS (µmhos), no further calculations are necessary. For instruments that require the use of a cell constant, a typical calculation is as follows:

$$\text{Specific conductance} = AB \quad , \mu S/cm \ ,$$

where

A = measured conductance, µS/cm,

B = constant for conductivity cell = 1.01.

7. Precision and Accuracy

7.1 Forty-one analysts in 17 laboratories analyzed six synthetic water samples containing increments of inorganic salts (Table 4.28-2).

Table 4.28-2. Data on the increments of inorganic salts in water samples

Increments	Precision		
Specific conductance (S/cm)	Standard deviation (S/cm)	Accuracy	
		Bias (%)	Bias (S/cm)
100	7.55	-2.02	-2.0
106	8.14	-0.76	-0.8
808	66.1	-3.63	-29.3
848	79.6	-4.54	-38.5
1640	106	-5.36	-87.9
1710	119	-5.08	-86.9

7.2 In a single laboratory, using surface water samples with an average specific conductivity of 536 S/cm at 25°C, the standard deviation was ± 6.

Working Bibliography for Sect. 4.28

ASTM Standards, Part 31, Water, p. 123, Method D1125-71 (1976).

Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 71, Method 205 (1975).

4.29 Determination of Nitrogen, Kjeldahl (Total), Spectrophotometric Method

(performed by Environmental Analysis Laboratory)

Source: *Environmental and Effluent Analysis Manual*, Union Carbide, Nuclear Division

1. Scope and Application

1.1 This method is used to determine total Kjeldahl nitrogen in drinking, surface and saline waters and in domestic and industrial wastes. The procedure converts nitrogen components of biological origin, such as amino acids, proteins, and peptides, to ammonia, but may not convert the nitrogenous compounds of some industrial wastes such as amines, nitro compounds, hydrazones, oximes, semi-carbazones, and some resistant tertiary amines.

1.2 The method is described for macro glassware; however, micro equipment may be used.

2. Summary of Method

2.1 The sample is heated in the presence of concd sulfuric acid (H_2SO_4), potassium sulfate (K_2SO_4) and mercuric sulfate ($HgSO_4$) and evaporated until SO_3 fumes are obtained and the solution becomes colorless or pale yellow. The residue is cooled, diluted, and made alkaline with hydroxide-thiosulfate solution. The ammonia is distilled and determined spectrophotometrically after Nesslerization.

2.2 The nitrogen found by this method is defined as total Kjeldahl nitrogen (TKN). It includes free ammonia and organic nitrogen compounds that are converted to ammonium sulfate by the digestion. Organic nitrogen may be calculated by subtracting the free ammonia nitrogen value (Nitrogen, Ammonia, Procedure 4.21) from the total Kjeldahl nitrogen value.

2.3 The lowest concentration reported, using a 500-ml sample, is 0.2 mg/liter.

3. Sample Handling and Preservation

3.1 Samples may be preserved by the addition of 2 ml of concd H_2SO_4 or 40 mg $HgCl_2$ per liter and stored at 4°C. Even when preserved in this manner, conversion of organic nitrogen to ammonia may occur. Preserved samples should be analyzed as soon as possible.

4. Apparatus

4.1 Kjeldahl digestion flasks, 800-ml

4.2 Distillation apparatus: Kjeldahl flask, Kjeldahl bulb, condenser, and rubber stoppers for connecting apparatus.

4.3 Spectrophotometer, for use at 425 nm

4.4 Spectrophotometer cells, with light path of 1 cm or longer

5. Reagents

5.1 All distilled water used should be ammonia free. This is best prepared by passing distilled water through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Operate and regenerate the column according to the manufacturer's instructions.

5.2 Mercuric sulfate solution ($HgSO_4$): Dissolve 8 g red, mercuric oxide (HgO) in 50 ml of 1:5 sulfuric acid (10.1 ml concd H_2SO_4: 40 ml distilled water) and dilute to 100 ml with distilled water. (1 ml = 0.08 g $HgSO_4$)

5.3 Sulfuric acid-mercuric sulfate-potassium sulfate solution: Dissolve 267 g K_2SO_4 in 1300 ml distilled water and 400 ml concd H_2SO_4. Add 50 ml $HgSO_4$ solution (step 5.2) and dilute to 2 liters with distilled water. (1 liter = 133.5 g K_2SO_4 and 4.0 g $HgSO_4$)

5.4 Sodium hydroxide-sodium thiosulfate solution: Dissolve 500 g NaOH and 25 g $Na_2S_2O_3 \cdot 5H_2O$ in distilled water and dilute to 1 liter.

5.5 Boric acid solution: Dissolve 20 g boric acid (H_3BO_3) in water and dilute to 1 liter with distilled water. (1 liter = 20 g H_3BO_3)

5.6 Ammonium chloride (NH_4Cl), stock solution: 1.0 ml = 1.0 mg ammonia nitrogen (NH_3-N). Dissolve 3.819 g NH_4Cl in distilled water and bring to volume in a 1 liter volumetric flask.

5.7 Ammonium chloride (NH_4Cl), standard solution: 1.0 ml = 0.01 mg. Dilute 10.0 ml of stock solution (step 5.6) to 1 liter in a volumetric flask.

5.8 Nessler reagent: Dissolve 100 g of mercuric iodide (HgI_2) and 70 g of potassium iodide (KI) in a small amount of water. Add this mixture slowly, while stirring, to a cooled solution of 160 g of NaOH in 500 ml of water. Dilute the mixture to 1 liter. If this reagent is stored in a Pyrex bottle out of direct sunlight, it will remain stable for a period of up to 1 year.

6. Calibration

6.1 Prepare several standards by taking suitable aliquots from the ammonia nitrogen (NH_3-N) standard solution(s), adding 1 ml of Nessler reagent and diluting to 50 ml in volumetric flasks. After 20 min read the absorbances of these solutions in the spectrophotometer against a blank solution. From the values obtained, plot absorbance versus mg NH_3-N for the standard curve. Values of standards chosen should encompass the range expected for the samples. The selection of cell path-length should be governed by the amount of NH_3-N in the samples.

7. Procedure

7.1 Place 500 ml of sample or a suitable aliquot into an 800-ml Kjeldahl flask. If an aliquot less than 500 ml is used, dilute to 500 ml with distilled water.

7.2 Add 100 ml sulfuric acid-mercuric sulfate-potassium sulfate solution (step 5.3) and evaporate the mixture in the Kjeldahl flask until SO_3 fumes are given off and the solution turns colorless or pale yellow. Continue heating for 30 additional min. Cool the residue and add 300 ml distilled water.

7.3 Make the digestate alkaline by careful addition of 100 ml of sodium hydroxide-thiosulfate solution (step 5.4) without mixing. Slow addition of the dense caustic solution down the tilted

neck of the digestion flask will cause the heavier solution to underlay the aqueous H_2SO_4 solution without loss of free ammonia. Do not mix until the digestion flask has been connected to the distillation apparatus.

7.4 Connect the Kjeldahl flask to the condenser with the tip of the condenser below the level of the H_3BO_3 solution (step 5.5) in the receiving flask.

7.5 Distill 300 ml, at the rate of 6 to 10 ml/min, into 50 ml of 2% H_3BO_3 contained in a 500-ml Erlenmeyer flask. Dilute the distillate to 500 ml.

7.6 Pipette an aliquot of the distillate into a 50-ml volumetric flask, add 1 ml of Nessler reagent, dilute to volume with distilled water, mix, and allow 20 min for full color development. Measure the absorbance of the solution at 425 nm against a reagent blank. For highest accuracy, the reagent blank should represent ammonia obtained by carrying distilled water and reagents through the digestion and distillation operations. Using the absorbance values, obtain the nitrogen content from the standard calibration curve.

8. Calculations

8.1 Total Kjeldahl nitrogen = $\frac{AB \times 1000}{VC}$, mg/liter,

where

A = nitrogen reading from standard curve, mg,
B = final volume of distillate collected, ml,
C = distillate taken for Nesslerization, ml,
V = volume of samples used, ml.

8.2 Organic Kjeldahl nitrogen (OKN). OKN = TKN - (NH_3-N) (as determined by Procedure 4.21).

9. Precision and Accuracy

9.1 Thirty-one analysts in 20 laboratories analyzed natural water samples containing exact increments of organic nitrogen. (Table 4.28-3).

Table 4.29-3. Data on the increments of organic nitrogen in water samples

Increment	Precision	Accuracy	
Nitrogen, Kjeldahl (mg/liter)	Standard deviation (mg/liter)	Bias (%)	Bias (mg/liter)
0.20	0.197	+15.54	+0.03
0.31	0.247	+ 5.45	+0.02
4.10	1.056	+ 1.03	+0.04
4.61	1.191	- 1.67	-0.08

Working Bibliography for Sect. 4.29

Manual of Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, p. 175 (1976).

Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 437, Method 421 (1975).

4.30 Determination of Fecal Coliform Bacteria by Direct Count Method

(performed by Environmental Analysis Laboratory)

Source: *Evironmental and Effluent Analysis Manual,* Union Carbide, Nuclear Division

1. Scope and Application

   1.1 This test determines the fecal coliform density in various types of water samples, especially sewage plant effluents.

   1.2 The presence of coliform bacteria in water is a warning sign that other dangerous bacteria may be present.

2. Summary of Method

   2.1 A sample is filtered through a membrane filter, and the filter is placed in contact with an enriched lactose medium. After incubation for 24 h at 44.5°C ± 0.2°C, the coliform colonies are counted directly under a microscope. The coliform density is reported as colonies/100 ml of sample.

   2.2 The lowest concentration reported, when a sample size selected from Table 4.28-1 in step 5.6.1 is used, is 1 colony/100 ml.

3. Sample Handling and Preservation

   3.1 Containers.

   Samples for bacteriologic examination must be collected in bottles that have been cleansed and rinsed with great care, given a final rinse with distilled water, and sterilized.

   3.2 Dechlorination.

   3.2.1 A dechlorinating agent should be added to bottles intended for the collection of water containing residual chlorine. Sodium thiosulfate ($Na_2S_2O_3$) is a satisfactory dechlorinating agent. Its presence at the instant of collection of a sample from a chlorinated supply will neutralize any residual chlorine and will prevent a continuation of the bactericidal action of the chlorine during the time the sample is in transit to the laboratory. The bacteriologic examination will then indicate more

probably the true bacterial content of the water at the time of sampling.

3.2.2 The sodium thiosulfate ($Na_2S_2O_3$) should be added to the clean sample bottle before sterilization in an amount sufficient to provide an approximate concentration of 100 mg/liter in the sample. This can be accomplished by adding 0.1 ml of 10% $Na_2S_2O_3$ to a 120-ml (4 oz) bottle. (This will neutralize a sample containing about 15 mg of residual chlorine per liter.) The bottle is then stoppered, capped, and sterilized by either dry or moist heat.

3.3 Metal complexation.

Water samples high in copper or zinc and wastewater samples high in heavy metals should be collected in sample bottles containing a chelating agent that will reduce metal toxicity. This is particularly significant when such samples are in transit for 24 h or more. Ethylene-diaminetetraacetic acid (EDTA) is a satisfactory chelating agent. A concentration of 372 mg/liter has been found adequate. The EDTA may be added separately to the sample bottle before bottle sterilization (0.3 ml of a 15% solution in a 120-ml bottle) or it may be combined with the $Na_2S_2O_3$ solution before addition.

4. Apparatus and Reagents

4.1 Sterile membrane filter, grid marked, millipore filter HA type, 47 mm in diam., 0.45 μ-pore size (Hydrosol type)

4.2 Sterile absorbent pads for nutrient

4.3 Sterile culture container (15- by 60-mm petri dishes, glass), borosilicate or equivalent grade, or 50- by 12-mm plastic, disposable sterile petri dishes with tight-fitting lids

4.4 Sterile 10-ml pipettes, graduated in 1 ml

4.5 Sterile 1-ml pipettes, graduated in 0.1 ml

4.6 Pipette boxes, stainless steel or aluminum (sterilize pipettes in boxes with cover off)

4.7 Milk dilution bottle, Pyrex brand, graduated at 99 ml for dilution water. Preferable screw-cap type

4.8 Sterile funnel apparatus, Millipore filter holder No. xx2004720, a complete hydrosol stainless steel holder

4.9 Dissecting microscope, with 10X or 15X magnification, wide-field binocular with fluorescent lamp

4.10 Steam autoclave, with approved gauges

4.11 Source of vacuum

4.12 Alcohol or gas burner

4.13 Forceps with smooth flat inner surface, not sharp on the edges or corners (Millipore Filter Corporation Catalog No. XX62 00 6)

4.14 Drying oven, with thermostat and thermometer, able to reach and maintain a temperature of at least 170°C.

4.15 Sample bottles, autoclavable 4-oz screw cap polypropylene, Nalgene #2105

4.16 Incubation water bath with cover to maintain a temperature of 44.5°C ± 0.2°C

4.17 Whirl Pak bags, 18-oz size

4.18 M-FC broth base, Difco 0883-02

4.19 Bacto-rosolic acid, Difco No. 3228-09

4.20 Alcohol

5. Procedure

5.1 Sterilization of equipment.

5.1.1 Wash all glassware and filtering equipment using a suitable detergent. Rinse thoroughly with tap water, then distilled water, and dry. The surfaces should be free of any residue.

5.1.2 Sterilize glassware not in metal containers by dry heating for not less than 60 min at 170°C. Sterilize pipettes in metal containers for not less than 2 h at 170°C.

5.1.3 Membrane filters are conveniently packaged in units of 10, sterilized, and ready for use. The packets also contain 10 sterilized absorbent pads.

5.1.4 Autoclave the 99-ml dilution bottles after filling to 102 ml with buffered dilution water.

5.1.4.1 Screw caps on loosely and place bottles upright in a basket or suitable holder; cover with heavy brown kraft paper.

5.1.4.2 Autoclave for 20 min at 121°C and 1.04 x 10^5 Pa (15 psi). Start timing when autoclave has reached the proper temperature and pressure.

5.1.4.3 Turn off steam supply after 20 min and allow autoclave to cool slowly.

5.1.4.4 When the pressure reaches zero, remove the bottles from the autoclave.

5.1.5 Sterilize the funnel and base. Wrap each separately in kraft paper and autoclave for 15 min at 121°C and 1.04 x 10^5 Pa (15 psi).

5.1.6 Sterilize the forceps used for handling sterile filters.

5.1.6.1 Place the tip of the forceps into a 50-ml beaker containing a 1-in. level of alcohol.

5.1.6.2 Light the alcohol or gas burner.

5.1.6.3 Remove the forceps from the beaker and place the tip over the flame source just long enough to ignite the alcohol. Do NOT prolong heating.

5.1.6.4 The forceps are sterile and ready to use as soon as the alcohol on the forceps is consumed and the flame is out.

5.2 Preparation of buffered water.

5.2.1 Weight 34 grams of potassium phosphate, monobasic (KH_2PO_4), into 500 ml of distilled water.

5.2.2 Adjust the pH to 7.2 with 1 N NaOH and dilute to 1 liter with distilled water. This is the stock phosphate buffer solution and should be stored under refrigeration.

5.2.3 Add 1.25 ml of the stock phosphate buffer solution to 1 liter of distilled water. Dispense 102 ml of this buffered water into a dilution bottle to provide 99 ml after autoclaving for 20 min.

5.3 Preparation of culture medium.

5.3.1 Dissolve 1 g of bacto-rosolic acid in 100 ml of 0.2 N NaOH. This solution may be kept under refrigeration for approximately 14 days at 2 to 10°C. It should be discarded if its color changes from dark red to muddy brown.

5.3.2 Add 1 ml of the rosolic acid solution to exactly 100 ml of sterile distilled water and pour into a sterile 250-ml screw cap flask.

5.3.3 Weigh 3.7 g of the M-FC broth base and add to the water-rosolic acid solution. (Proportional amounts of medium may be prepared, that is, 1.8 g of broth base to 50 ml of water.)

5.3.4 Heat the flask and contents on a hot plate or flame and shake the flask occasionally to assure dissolution.

5.3.5 Heat to the boiling point, remove promptly from the heat, and cool to below 45°C. The cooled solution should have a dark cherry color and may be stored at 2 to 10°C for as long as 96 h, after which it should be discarded.

5.3.6 A commercially prepared culture medium, packaged in 2-ml glass ampules, may be purchased from the Millipore Corporation, Bedford, Massachusetts under catalog number M 0000002F.

5.4 Preparation of petri dishes for receiving membranes.

5.4.1 Being careful to avoid contamination, label the sterile petri dishes with sample numbers corresponding to those on a work sheet.

5.4.2 Place a sterile absorbent pad into each labeled dish and deposit 2 ml of prepared culture medium onto the pad.

5.4.3 Pour off the excess medium when the pad appears to be fully saturated.

5.5 Preparation of filter apparatus.

5.5.1 Connect two suction flasks in series using one for the filter receptacle and the other to protect the vacuum

from water being pulled in accidentally. Connect the train to a source of vacuum with a length of vacuum hose.

5.5.2 Unwrap a sterilized funnel, being careful not to contaminate it, and place it on a ring stand.

5.5.3 Unwrap a sterilized filter receptacle and place it on the suction flask.

5.5.4 Place a sterile filter on the filter receptacle, center it properly, and then place the funnel on the filter receptacle.

5.6 Preparation of sample.

5.6.1 Select the proper sample size from Table 4.30-1.

Table 4.30-1. Quantity of water used for different sources

	Volume to be filtered[a] (ml)						
Water source[b]	100	50	10	1	0.1	0.01	0.001
Lakes, reservoirs	X	X					
Wells, springs	X	X					
Water supply, intake		X	X	X			
Natural bathing waters		X	X	X			
Sewage treatment plant, secondary effluent			X	X	X		
Farm ponds, rivers				X	X	X	
Stormwater runoff				X	X	X	
Raw municipal sewage					X	X	X
Feedlot runoff					X	X	X

[a]Samples of less than 1 ml should be diluted before filtering.

[b]Where no sample history is available, 4-ml, 10-ml, and 30-ml samples are used.

5.6.2 Sample dilution (if necessary).

5.6.2.1 Shake the bottle containing the sample 25 times to assure adequate mixing; remove the top and flame the mouth of the bottle to sterilize it.

5.6.2.2 Remove the screw cap from a sterile dilution bottle containing 99 ml of sterile dilution water and flame the mouth of the bottle.

5.6.2.3 Using a sterile pipette, transfer exactly 1 ml of sample into the 99 ml of dilution water. Flame the mouth of the dilution bottle and carefully replace the cap.

5.6.2.4 Shake the bottle 25 times. Remove the cap and flame the mouth of the bottle again.

5.6.2.5 With the vacuum turned off, pour 25 to 30 ml of sterile buffered water into the funnel to provide a better distribution of the sample over the surface of the filter.

5.6.2.6 Using a sterile 1-ml pipette, transfer exactly 1 ml of sample from the dilution bottle onto the filter. At this point, 0.01 ml of the original sample has been processed.

5.6.2.7 If additional dilution is required, transfer 1 ml of solution from the first dilution bottle to a second sterile dilution bottle and proceed from step 5.6.2.4.

5.6.2.8 Carefully remove the filter paper from funnel and place it into a prepared petri dish (step 5.4.2). Make certain that good contact is made between the filter paper and the sterile absorbent pad.

5.6.2.9 Between samples, sterilize the funnel and base by immersing it in boiling water for 1 min and cooling it before use.

5.7 Incubation.

5.7.1 Place all prepared cultures in the water bath within 30 min after filtration.

5.7.2 Place four or five plates into an 18-oz. Whirl-Pak bag, making sure to trap as little air as possible when rolling the bag closed.

5.7.3 Roll the top a minimum of three times and fold the wired tabs to maintain water-tight conditions in the bag.

5.7.4 Submerge the bag, with the plates upside down, in the water bath incubator at 44.4°C ± 0.2°C for 24 h.

5.8 Counting.

5.8.1 Place the filter membrane in the field of the 10 to 15X microscope. Adjust the light source from above and perpendicular to the plane of the membrane to reflect light across the membrane.

5.8.2 Count all colonies having a blue color as fecal coliforms. The nonfecal coliform colonies are gray to cream-colored. Normally, few nonfecal coliform colonies will be observed because of the selective action of the elevated temperature and the addition of the rosolic acid salt reagent.

5.8.3 Record colonies counted on each filter on an appropriate data sheet.

6. Calculation

Calculate the fecal coliform density as follows:

$$\text{Coliform colonies/100 ml} = \frac{A \times 100 \text{ ml}}{B}$$

where

A = coliform colonies counted

B = volume of sample filtered, ml.

7. Multiple Tube Fermentation Method

7.1 The multiple tube fermentation method can be used as an alternative to the membrane filter technique described in this procedure.

The multiple tube method may be more desirable for chlorinated sewage effluents. (See *Standard Methods for the Examination of Water and Wastewater*, p. 916.)

Working Bibliography for Sect. 4.30

ASTM Standards, Part 31, Designation F-60-73, pp. 730-734 (1974).

Standard Methods for the Examination of Water and Wastewater, 14th ed., Method No. 908A, p. 916 and pp. 937-939 (1975).

Appendix A

Appendix A

ENVIRONMENTAL DATA

TYPE (1)	AM NO. (2-3)	WEEK NO. (4-5)	DATE ON MO. (6-7)	DATE ON DAY (8-9)	TIME ON (10-11)	DATE OFF MO. (12-13)	DATE OFF DAY (14-15)	TIME OFF (16-17)	CFM[1] (18-20)	CFM[2] (21-23)
F / G										

10^{-6} μC α (24-29)	10^{-6} μC β (30-35)	PARTICLE ACTIVITY RANGE d/24 hrs: < 10^5 (36-40)	10^5 - 10^6 (41-45)	10^6 - 10^7 (46-50)	> 10^7 (51-55)

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(3 4-64)

Air filters and the Environmental Data Cards are collected weekly from the local, perimeter, and remote air monitoring stations. The flow rate (cfm) date on/off, and time on/off are recorded on the card. The date on and time on should correspond to the previous week's date off and time off. A new card is left at the station with the date on, time on, and the flow rate (cfm) recorded. The Environmental Data Card will be completed by the technician conducting the analysis. The time is recorded to the nearest hour. The time interval of 7:30 to 8:29 is considered as the eighth hour; the interval of 8:30 to 9:29 is considered as the ninth hour.

Data from the analysis of the gummed papers are also recorded on Environmental Data Cards. The date on/off, time on/off, and the analysis from the Bio-Assay Laboratory are recorded on the card.

Samples are collected weekly, monthly, semiannually, and annually by technicians from the ESE Section. The analyses of these samples are conducted by technicians from other laboratories. Before submitting samples for analysis, a Request for Control Analysis Form must be completed and signed. For charcoal samples, the partially completed form that follows here can be used.

The circular chart utilized at the Gallaher and Melton Hill water stations is approximately 30 x 30 cm and is changed weekly. The actual flow of water is recorded on the chart. When installing the chart, the technician should record the station name, date on, time on, and his

REQUEST FOR CONTROL ANALYSIS

THIS FORM IS TO BE USED ONLY FOR SAMPLES CONTAINING LESS THAN 50 MILLIGRAMS CONCENTRATION OF FISSIONABLE MATERIAL.

CONTROL NO.

DATA REPORT TO			BUILDING NO.	SERIES NO.
DATE SUBMITTED	TELEPHONE NO.		CHARGE NO.	

SAMPLE CODE		DESIRED ANALYSIS	ESTIMATION OF CONCENTRATION	PREVIOUS HISTORY OF SAMPLE	NATURE AND ESTIMATION OF ACTIVITY	CONCENTRATION OF ALL CONSTITUENTS IN SAMPLE

Sample(s) contain_____g of Fissile Mtrl. (est)

Return to sender or dispose according to H.P. Manual.

REQUESTER

UCN-1910
(3 6-71)

REQUEST FOR CONTROL ANALYSIS

THIS FORM IS TO BE USED ONLY FOR SAMPLES CONTAINING LESS THAN 50 MILLIGRAMS CONCENTRATION OF FISSIONABLE MATERIAL.

CONTROL NO.

DATA REPORT TO | BUILDING NO. 4500 S | SERIES NO.

DATE SUBMITTED | TELEPHONE NO. 4-6669 | CHARGE NO. 3195

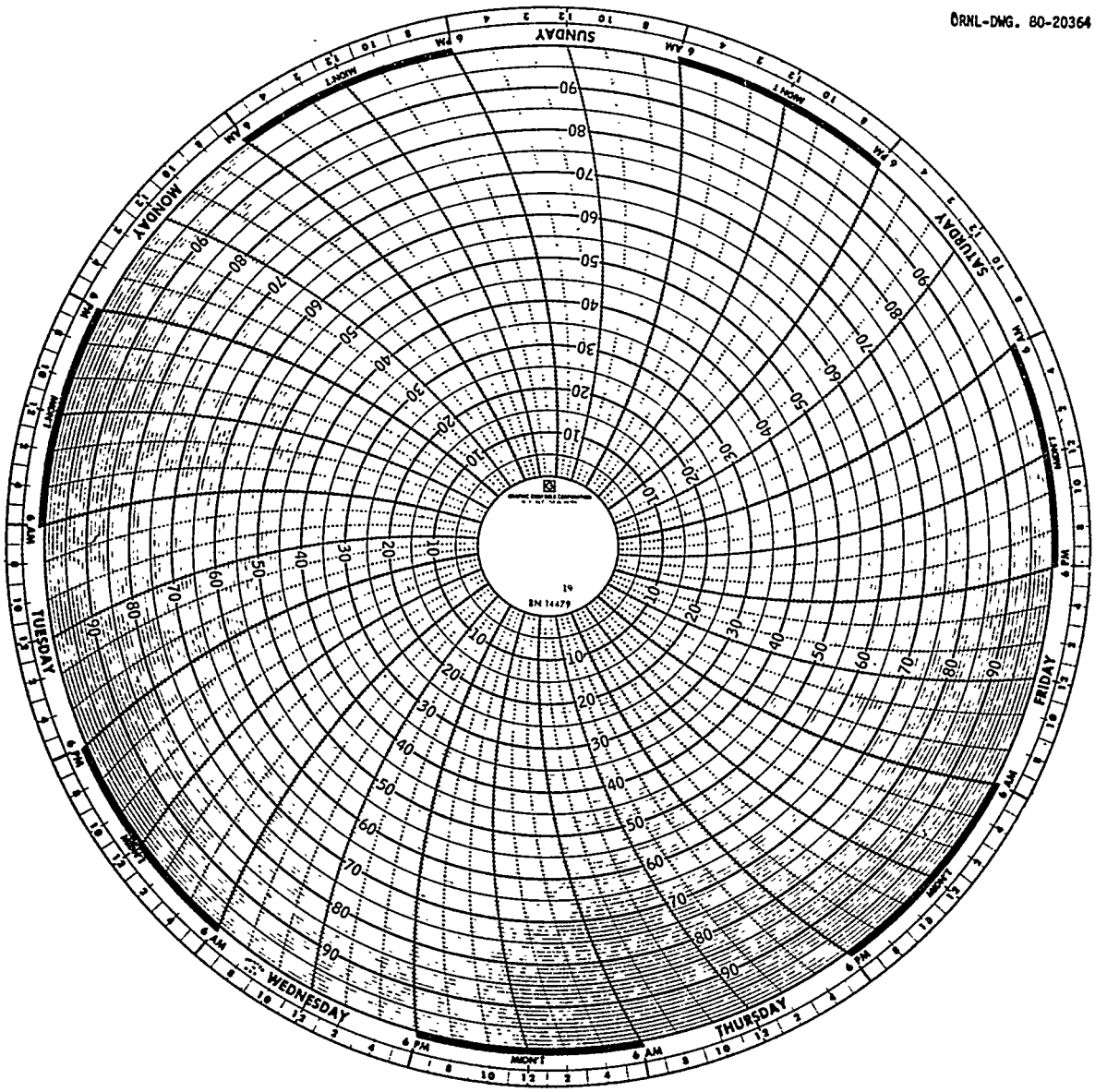
SAMPLE CODE		DESIRED ANALYSIS	ESTIMATION OF CONCENTRATION	PREVIOUS HISTORY OF SAMPLE	NATURE AND ESTIMATION OF ACTIVITY	CONCENTRATION OF ALL CONSTITUENTS IN SAMPLE
L-3	SW 1000				CHARCOAL FILTERS	
L-4	NSB					
L-6	SE 3027				DESIRED ANALYSIS, ^{131}I	
L-7	E 7001					
L-8	ROCK QUARRY					
L-9	NBVR				LAMS:	
L-10	W 2075				ON: OFF:	
L-16 L-20	E 4500 HFIR					
P-23	Walker Branch					
P -31	Kerr Hollow				PAMS: ON:	
P-32	Midway				OFF:	
P-33	Gallaher					
P-34	W.O.D.					
P-35	Blair					
P-36	Turnpike					
P-37 P-38	Hickory Cr. EGCR					
P-39	TOWNSITE					

Sample(s) contain_____g of Fissile Mtrl. (est)

Return to sender or dispose according to H.P. Manual.

REQUESTER

UCN-1010
(3 6-71)



initials on the chart. The old chart should have the above information plus the date off, time off, the total time in minutes when samples were taken, the number of samples taken, volume of water collected, and the technician's initials. The lake level should also be recorded for the Gallaher water station. This information is recorded by the technician on an Environs Monitoring Water Sample Collection Data Sheet and filed in the DEM office.

ORNL-DWG. 80-20365

_____
(Date)

ENVIRONS MONITORING
WATER SAMPLE COLLECTION DATA

Sampling Station:

- ☐ WOD
- ☐ MWOC
- ☐ MH
- ☐ GA
- ☐ CF

Period of Sampling:

Start _____ (month), _____ (day), _____ (hr)

End _____ (month), _____ (day), _____ (hr)

Sample Volume Collected:

Total inches in drums _____

or jugs _____

Liters collected _____

Sample Volume Delivered to Lab:

- ☐ The total collected
- ☐ Other _____

Condition of Sampler During Period:

- ☐ OK
- ☐ Other _____

Condition of Recorders (MH, WOD, GA):

- ☐ OK
- ☐ Other _____

Register Readings (MH & GA):

Counter setting _____

No. of samples _____

Sampling time _____

Range of Rainfall During Period (MH, WOD, GA):

- ☐ Little
- ☐ Moderate
- ☐ Much

Inches at MH _____

RAIN WATER DATA

TYPE	AM NO.	WEEK NO.	DATE ON		TIME ON	DATE OFF		TIME OFF	RAINFALL (IN.)
			MO.	DAY		MO.	DAY		
(1)	(2-3)	(4-5)	(6-7)	(8-9)	(10-11)	(12-13)	(14-15)	(16-17)	(18-22)
R									

10^{-6} μc β	
SOLUBLE (23-28)	INSOLUBLE (29-34)

UCN-5656
(3 4-64)

The volume of rainwater collected weekly depends on the rainfall within this period. The data for each sample collected at a local, perimeter, or remote air monitoring station are recorded on a Rain Water Data Card. The data include the date on/off, air monitoring station number, rainfall in inches, and the gross-beta count.

ATMOSPHERIC ACTIVITY

AM NO.	WEEK NO.	DATE ON		DATE OFF		CFM	FILTER		
		MO.	DAY	MO.	DAY		10^{-6} μcα	10^{-6} μcβ	PARTICLES
(2-3)	(5-6)	(8-9)	(11-12)	(14-15)	(17-18)	(20-22)	(24-28)	(30-34)	(36-38)
									*

GUMMED PAPER		IODINE	RAIN		
10^{-6} μcβ	PARTICLES	D/M	CC/SAMPLE	10^{-6} μcβ	RAINFALL (IN.)
(40-44)	(46-48)	(50-55)	(57-60)	(62-66)	(68-72)
	*	*	*		

UCN-11075
(3 3-74)

* ENTER NEGATIVE NUMBER IF NO SAMPLE

The data on air filters, gummed papers, and rain water are transferred from the Environmental Data Cards and Rain Water Cards to Atmospheric Activity Cards.

DATA CARD FOR MILK AND WATER SAMPLES

Date and Time Analyzed		
Reagent Bkg. (c/m)		
Process Efficiency (%)		
Counter Number		
Bkg. of Counter (c/m)		
Efficiency Factor		
Date and Time - Start		
Stop		
Total Counts		
Counting Time (min)		
Gross c/m		
Total Bkg. c/m		
Net c/m		
d/m/aliquot		
d/m/sample		

LABORATORY SAMPLE NO.

TYPE ANALYSIS

SAMPLE VOLUME

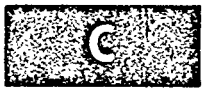
VOLUME ANALYZED

REMARKS

UCN-2716A
(3 10-72)

Milk and water samples are collected weekly by a technician from the DEM and analyzed by a technician in the Bio-Assay Laboratory. Prior to submitting the samples to the Bio-Assay Laboratory, the station, sample number, volume, and analysis desired are recorded on the cards. The cards are completed by a technician in the Bio-Assay Laboratory.

Effective Jan. 1, 1980, the Environmental Monitoring QA (Quality Assurance) Cards will be used. The information used for the data sheet is applicable to the Environmental Monitoring QA Collection Card (C). Other pertinent data are recorded on the SP-Storage-Preparation, AP — Analytical Processing, AA — Analytical Analysis, SC — Sample Counting, and DI — Data Interpretation Cards. The data are presented to the DEM's consultant from the Computer Sciences Division, who records it on computer tapes. For a detailed description of the QA Program, refer to *Quality Assurance Procedures for Environmental and Evaluation Surveillance Section at ORNL*, ORNL/TM-7213 (in preparation).



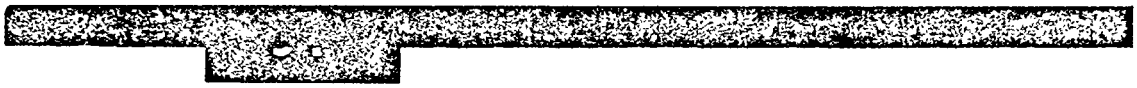
UCN-13637
(3 8-79)

Sample No.					
1	2	3	4	5	6

ENVIRONMENTAL MONITORING QA

Step	Type	Location	Count Rate		Time In					Time Out				
			On	Off	Yr.	Mo.	Day	Hr.	Min.	Yr.	Mo.	Day	Hr.	Min.
7 8	9 10	11 12 13 14 15	16 17 18 19	20 21 22 23	24 25	26 27	28 29	30 31	32 33	34 35	36 37	38 39	40 41	42 43
C														

Flow Rate On	Flow Rate Off	Comments	Special	Tech.	Init.
44 45 46	47 48 49	50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74	75	76 77	78 79 80



ENVIRONMENTAL MONITORING QA

Sample No.						Step	
1	2	3	4	5	6	7	8
						S	P

Time In					Time Out				
Yr.	Mo.	Day	Hr.	Min.	Yr.	Mo.	Day	Hr.	Min.
24 25	26 27	28 29	30 31	32 33	34 35	36 37	38 39	40 41	42 43

Comments	Special	Tech.	Init.
50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74	75	76 77	78 79 80

UCN-13638
(3 7-79)

ENVIRONMENTAL MONITORING QA

Sample No.						Step	
1	2	3	4	5	6	7	8
						A	P

Time In					Time Out				
Yr.	Mo.	Day	Hr.	Min.	Yr.	Mo.	Day	Hr.	Min.
24 25	26 27	28 29	30 31	32 33	34 35	36 37	38 39	40 41	42 43

Comments	Special	Tech.	Init.
50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74	75	76 77	78 79 80

UCN-13639
(3 8-79)

SP AA

ENVIRONMENTAL MONITORING QA

Sample No.						Step	
1	2	3	4	5	6	7	8
						A	A

Time In					Time Out				
Yr.	Mo.	Day	Hr.	Min.	Yr.	Mo.	Day	Hr.	Min.
24 25	26 27	28 29	30 31	32 33	34 35	36 37	38 39	40 41	42 43

Special

Comments			Tech.	Init.	
50 51 ... 74	75		76 77	78 79	80

UCN-13640
(3 8-79)

SP SC

ENVIRONMENTAL MONITORING QA

Sample No.						Step	
1	2	3	4	5	6	7	8
						S	C

Time In					Time Out				
Yr.	Mo.	Day	Hr.	Min.	Yr.	Mo.	Day	Hr.	Min.
24 25	26 27	28 29	30 31	32 33	34 35	36 37	38 39	40 41	42 43

Special

Comments			Tech.	Init.	
50 51 ... 74	75		76 77	78 79	80

UCN-13641
(3 8-79)

SP

ENVIRONMENTAL MONITORING QA

Sample No.						Step	
1	2	3	4	5	6	7	8
						D	I

Time In					Time Out				
Yr.	Mo.	Day	Hr.	Min.	Yr.	Mo.	Day	Hr.	Min.
24 25	26 27	28 29	30 31	32 33	34 35	36 37	38 39	40 41	42 43

Special

Comments			Tech.	Init.	
50 51 ... 74	75		76 77	78 79	80

UCN-13642
(3 8-79)

Units on the White Oak Dam Stage Gauge Chart Reader	3.87		3.87
	3.65		4.10
	3.42		4.33
	3.23		4.58
	3.02		4.81
	2.82		5.06
	2.63		5.33
	2.44		5.58
	2.25		5.85
	2.08		6.09
	1.92		6.36
	1.76		6.67
	1.61		6.91
	1.46		7.22
	1.31		7.52
	1.19		7.77
	1.06	1.12	8.07
	.942	1.00	8.32
	.832	.887	8.62
	.715	.771	8.93
	.606	.660	9.23
	.514	.559	
	.422	.468	
	.342	.382	
	.263	.302	
	.195	.229	
	.134	.165	

The flow of water through the weir of White Oak Dam (cfs) is recorded on linear recording chart paper. The volume of water can be determined with the aide of the White Oak Dam Stage Gauge Chart Reader which converts the flow to 10^{10} ml/6 h. The flow values of an inclining curve range from 0.134 to 3.87 10^{10} ml/6 h; the declining curve flow values range from 3.87 to 9.23 10^{10} ml/6 h. If the flow values are higher than 9.23 10^{10} ml/6 h, the highest value from the United States Department of Interior Geological Survey (198 cfs at 750 ft or the top of the gate) and the corresponding discharge value per foot are summed. The results are converted to 10^{10} ml/6 h.

UNITED STATES DEPARTMENT OF THE INTERIOR

Geological Survey (Water Resources Division)

Rating table for White Oak Creek at White Oak Dam
May 7, 1963 (flow through upper gate only)

Gate at 744.0
Rating No. 3

Gauge height feet	Discharge cfs	Difference cfs	Gauge height feet	Discharge cfs	Difference cfs	Gauge height feet	Discharge cfs	Difference cfs	Gauge height feet	Discharge cfs	Difference cfs
4.0	.0	.03	.06	.09	.12	.15	.18	.21	.24	.27	.3
.1	.3	.35	.40	.45	.50	.55	.60	.65	.70	.75	.5
.2	.8	.86	.92	.98	1.04	1.10	1.16	1.22	1.28	1.34	.6
.3	1.4	1.48	1.56	1.64	1.72	1.80	1.88	1.96	2.04	2.12	.8
.4	2.2	2.30	2.40	2.50	2.60	2.70	2.80	2.90	3.00	3.10	1.0
.5	3.2	3.31	3.42	3.53	3.64	3.75	3.86	3.97	4.08	4.19	1.1
.6	4.3	4.43	4.56	4.69	4.82	4.95	5.08	5.21	5.34	5.47	1.3
.7	5.6	5.73	5.86	5.99	6.12	6.25	6.38	6.51	6.64	6.77	1.3
.8	6.9	7.05	7.20	7.35	7.50	7.65	7.80	7.95	8.10	8.25	1.5
.9	8.4	8.55	8.70	8.85	9.00	9.15	9.30	9.45	9.60	9.75	1.5
5.0	9.9	10.08	10.3	10.4	10.6	10.8	11.0	11.2	11.3	11.5	1.8
.1	11.7	11.9	12.1	12.3	12.5	12.6	12.8	13.0	13.2	13.4	1.9
.2	13.6	13.8	14.0	14.1	14.3	14.5	14.7	14.9	15.0	15.2	1.8
.3	15.4	15.6	15.8	16.0	16.2	16.4	16.6	16.8	17.0	17.2	2.0
.4	17.4	17.6	17.8	18.0	18.2	18.4	18.7	18.9	19.1	19.3	2.1
.5	19.5	19.7	19.9	20.1	20.3	20.5	20.7	20.9	21.1	21.3	2.0
	21.5	21.7	22.0	22.2	22.5	22.7	22.9	23.2	23.4	23.7	2.4
.7	23.9	24.2	24.4	24.6	24.9	25.2	25.4	25.6	25.9	26.2	2.5
.8	26.4	26.6	26.9	27.1	27.4	27.6	27.8	28.1	28.3	28.6	2.4
.9	28.8	29.1	29.3	29.6	29.8	30.1	30.4	30.6	30.9	31.1	2.6
6.0	31.4	31.7	31.9	32.2	32.5	32.8	33.0	33.3	33.6	33.8	2.7
.1	34.1	34.4	34.7	34.9	35.2	35.5	35.8	36.1	36.3	36.6	2.8
.2	36.9	37.2	37.5	37.8	38.1	38.4	38.7	39.0	39.3	39.6	3.0
.3	39.9	40.2	40.5	40.9	41.2	41.5	41.8	42.1	42.5	42.8	3.2
.4	43.1	43.4	43.7	44.0	44.3	44.6	44.9	45.2	45.5	45.8	3.0
.5	46.1	46.4	46.8	47.1	47.5	47.8	48.1	48.5	48.8	49.2	3.4
.6	49.5	49.8	50.2	50.5	50.8	51.2	51.5	51.8	52.1	52.5	3.3
.7	52.8	53.1	53.4	53.8	54.1	54.4	54.7	55.0	55.4	55.7	3.2
.8	56.0	56.4	56.7	57.1	57.5	57.8	58.2	58.6	59.0	59.3	3.7
.9	59.7	60.1	60.4	60.8	61.2	61.6	61.9	62.3	62.7	63.0	3.7
7.0	63.4	63.8	64.1	64.5	64.8	65.2	65.6	65.9	66.3	66.6	3.6
.1	67.0	67.4	67.8	68.1	68.5	68.9	69.3	69.7	70.0	70.4	3.8
.2	70.8	71.2	71.6	72.0	72.4	72.8	73.3	73.7	74.1	74.5	4.1
.3	74.9	75.3	75.6	76.0	76.4	76.8	77.1	77.5	77.9	78.2	3.7
.4	78.6	79.0	79.4	79.9	80.3	80.7	81.1	81.5	82.0	82.4	4.2
.5	82.8	83.2	83.7	84.1	84.5	85.0	85.4	85.8	86.2	86.7	4.3
.6	87.1	87.5	87.9	88.4	88.8	89.2	89.6	90.0	90.5	90.9	4.2

UNITED STATES DEPARTMENT OF THE INTERIOR

Geological Survey (Water Resources Division)

Rating table for White Oak Creek at White Oak Dam (continued)

Gauge height feet	Discharge cfs	Difference cfs	Gauge height feet	Discharge cfs	Difference cfs	Gauge height feet	Discharge cfs	Difference cfs	Gauge height feet	Discharge cfs	Difference cfs
.7	91.3	91.7	92.2	92.6	93.0	93.4	93.9	94.3	94.7	95.2	4.3
.8	95.6	96.0	96.4	96.8	97.2	97.6	98.0	98.4	98.8	99.2	4.0
.9	99.6	100	100	101	101	102	102	103	103	104	4.4
8.0	104	104	105	106	106	106	107	108	108	108	5.0
.1	109	109	110	110	111	111	111	112	112	113	4.0
.2	113	114	114	114	115	116	116	116	117	118	5.0
.3	118	118	119	120	120	120	121	122	122	122	5.0
.4	123	123	124	124	125	125	125	126	126	127	4.0
.5	127	128	128	128	129	130	130	130	131	132	5.0
	132	132	133	133	134	134	134	135	135	136	4.0
.7	136	136	137	138	138	138	139	140	140	140	5.0
.8	141	142	142	142	143	144	144	144	145	146	5.0
.9	146	146	147	148	148	148	149	150	150	150	5.0
9.0	151	151	152	152	153	153	153	154	154	155	4.0
.1	155	156	156	156	157	158	158	158	159	160	5.0
.2	160	160	161	161	162	162	162	163	163	164	4.0
.3	164	164	165	166	166	166	167	168	168	168	5.0
.4	169	170	170	170	171	172	172	172	173	174	5.0
.5	174	174	175	175	176	176	176	177	177	178	4.0
.6	178	178	179	180	180	180	181	182	182	182	5.0
.7	183	184	184	184	185	186	186	186	187	188	5.0
.8	188	188	189	190	190	190	191	192	192	192	5.0
.9	193	194	194	194	195	196	196	196	197	198	5.0
10.0											

UNITED STATES
DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

Water Resources Division

Rating table for White Oak Creek at White Oak Dam near Oak Ridge, Tenn.
July 11, 1953 (for flow over the dam only)

Gauge height feet	Discharge cfs	Difference cfs	Gauge height feet	Discharge cfs	Difference cfs	Gauge height feet	Discharge cfs
0.00	0	12	2.00	510	30	4.00	1110
.10	12	16	.10	540		.10	1140
.20	28	20	.20	570		.20	1170
.30	48	22	.30	600		.30	1200
.40	70	22	.40	630		.40	1230
.50	92	23	.50	660		.50	1260
.60	115	25	.60	690		.60	1290
.70	140	25	.70	720		.70	1320
.80	165	25	.80	750		.80	1350
.90	190	25	.90	780		.90	1380
1.00	215	25	3.00	810		.00	1410
.10	240	30	.10	840		.10	1440
.20	270	30	.20	870		.20	1470
.30	300	30	.30	900		.30	1500
.40	330	30	.40	930		.40	1530
.50	360	30	.50	960		.50	1560
.60	390	30	.60	990		.60	1590
.70	420	30	.70	1020		.70	1620
.80	450	30	.80	1050		.80	1650
.90	480	30	.90	1080		.90	1680

Central Monitoring Station Panel

Description of Environs Monitoring Telemeter Panel

The panel has four multipoint Brown records; five single-point and one multipoint EA recorders. The data recorded are:

PAMs 1-6 and 9, air filter β-γ c/m;
LAMs 1-22, air filter β-γ c/m;
FOMs,[a] any 12 of 44, β-γ or α c/m;
Temperature, temperature gradient, and dew point;
Wind direction and velocity; and
White Oak Dam, effluent water, β-γ c/m.

Annunciated signals are:

PAMs — lighted annunciator panel for high β-γ count rate
LAMs — lighted annunciator panel, station indicator lamp, map display lamp, and signal to guard headquarters for high β-γ count rate and filter tape break
FOMs — lighted annunciator panel (if one of 12 selected monitors), monitor indicator lamp and map display lamp for high count rate
White Oak Dam Monitor — lighted annunciator panel and signal to guard headquarters for high count rate

Operators controls are:

PAMs — range multiplier selector switches
LAMs — range multiplier selector switches, filter change and telephone switches
FOMs — 12 patch cords for selecting monitors for recording.
Guard headquarters signal — timer and buttons for enabling or disabling and a button for testing
Acknowledge and reset buttons for the annunciator lights
Selector switches for single-point recording of PAMs and LAMs

Data Interpretation

Although any alarm signal should be considered valid until found determined otherwise, the telemetered signals are subject to much interference from faults in phone lines, particularly during thunderstorms and rainy weather.

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[a] FOMs — Fallout monitors.

The radioactivity in air may be expected to increase significantly from natural radioactivity during temperature inversions.

The activity detected at White Oak Dam is subject to buildup from material collected within the shield and on the detectors.

The fallout monitors may detect activity which is associated with particles too large to be collected by the air monitor.

Operating Procedures

General — To clear an annunciator signal, press the ACKNOWLEDGE button then observe if the high-level condition is indicated by the recorder. If not, press the RESET button and the signal should remain cleared. If the condition that caused the signal (high reading, tape break, etc.) still exists, the signal will not remain reset.

LAMs — High readings may be reduced at the recorder by switching to the X2 or X4 recorder range. The annunciator signal may be discontinued by switching the station to TELEPHONE. A new filter may be inserted momentarily by depressing the station switch to FILTER ADVANCE.

PAMs — High readings may be reduced by switching to the X2 or X4 recorder ranges.

FOMs — The annunciator signal is operated from the Brown recorder. A high-level condition may be discontinued from the annunciator by disconnecting the appropriate patch cord.

White Oak Dam Monitor — Presently there are no means of clearing a continuing signal condition at the panel except by clearing the condition at the dam.

Weather Instruments — There are no signals related to the weather instruments and no means of clearing a faulty condition.

Reporting

Any indication of significant activity which may be valid should be reported to and, on Department of Environmental Management off-shifts, and Radiation Survey Shift Supervisor.

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